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PB-287 129

Breakpoint Chlorination/Activated Carbon Treatment: Effect on Volatile Halogenated Organics

(U.S.) Municipal Environmental Research Lab, Cincinnati, OH

Sep 78

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-165	2.
3. RECIPIENT'S ACCESSION NO. PB287129	
4. TITLE AND SUBTITLE BREAKPOINT CHLORINATION/ACTIVATED CARBON TREATMENT: EFFECT ON VOLATILE HALOGENATED ORGANICS	5. REPORT DATE September 1978 (Issuing Date) 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) James J. Westrick, Michael D. Cummins and Jesse M. Cohen	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Wastewater Research Division, TPDB, P-CTS Municipal Environmental Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO. BC611, SOS#5, BE-10 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory-Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED In-House 6/76 - 1/78 14. SPONSORING AGENCY CODE EPA/600/14
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The production and removal of six volatile halogenated organic compounds during treatment of tertiary clarified and filtered wastewater by breakpoint chlorination and activated carbon was examined in a continuous flow pilot plant. Short contact time breakpoint chlorination of filter effluent increased chloroform and bromodichloromethane concentrations by 50 µg/1 and 10 µg/1, respectively. Treatment by carbon prior to chlorination reduced the formation of chloroform by a factor of four, but was less effective in reducing the amount of bromoform produced.

A 20-minute empty bed contact time activated carbon adsorber was much more efficient for chloroform removal than a 10-min adsorber, probably because of competitive effects of more strongly adsorbed organics. The removal of chloroform by the second stage carbon contactors conformed to an equilibrium expression of the Freundlich type.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chlorination - sewage treatment Activated carbon Halohydrocarbons Pilot Plants Ammonia	Breakpoint chlorination	13/B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 88
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC A05

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1978 — 757-140/1436

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-78-165
September 1978

Research and Development

PB 287129

EPA

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EPA-600/2-78-165
September 1978

BREAKPOINT CHLORINATION/ACTIVATED CARBON TREATMENT: EFFECT ON VOLATILE HALOGENATED ORGANICS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research, a vital communications link between the researcher and the user community.

This report summarizes the results of a pilot plant study investigating the formation and removal of six volatile, halogenated organic compounds in a tertiary breakpoint chlorination/activated carbon system.

Francis T. Mayo
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ABSTRACT

A continuous-flow pilot plant project was conducted with two major objectives: (1) to monitor the production of six volatile halogenated organic compounds during breakpoint chlorination of wastewater for ammonia removal and (2) to determine the efficiency of removal of these compounds by activated carbon.

The chlorination/activated carbon systems were operated on lime-clarified and filtered trickling filter effluent. One chlorination system was located before a two-stage carbon adsorber, and a second chlorination system was between stages of a second two-stage adsorber. Breakpoint chlorination increased the chloroform concentration from a median value of 11 µg/l in the tertiary filter effluent to a median value of 61 µg/l. Chloroform production in that system was about four times greater than that of the chlorination system located after one stage of carbon. Bromodichloromethane was formed in amounts usually less than 10 µg/l by chlorinating the filter effluent. Chlorination of the first stage carbon effluent produced lower concentrations of bromodichloromethane during the first month of operation, but these concentrations were later equal to or greater than those produced by chlorinating the filter effluent. Dibromochloromethane, bromoform, carbon tetrachloride and 1,2-dichloroethane were formed at very low concentrations, if at all.

A 20-min empty bed contact time adsorber was much more efficient for chloroform removal than a 10-min contact time adsorber, probably because of competitive effects of more strongly adsorbed organics. The removal of chloroform by the second stage carbon columns conformed to an equilibrium expression of the Freundlich type.

This report covers the period of operation from June 3, 1976, to August 9, 1976, and work was completed as of January 13, 1978.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the work of Patricia Kiraly, Arthur Turner and Michael Jelus who participated in the assembly and/or operation of the system. The efforts of E. Marco Aieta, Joseph Carvitti and Dirk Krouskop in pilot plant operation, data handling and special projects were instrumental to the success of this project. The contributions of the staff of the Waste Identification and Analysis Section, WRD, of the Municipal Environmental Research Laboratory, especially B. M. Austern, Caroline Madding and R. H. Wise are acknowledged with sincere thanks. Lawrence J. Kamphake was of invaluable assistance in developing and refining the pilot plant automated monitoring systems for ammonia and residual chlorine.

SECTION 1

INTRODUCTION

Breakpoint chlorination is a process that can be used to oxidize ammonia nitrogen to nitrogen gas and thus remove it from wastewaters. If breakpoint chlorination is followed by an activated carbon adsorption system, the carbon can accomplish both organic removal and dechlorination. The formation of halogenated methanes during the disinfection of drinking water supplies by application of small doses of chlorine to waters of relatively low organic strength is a recently documented problem facing the water supply industry. When ammonia is removed by breakpoint chlorination, large doses of chlorine are applied to wastewater, with its relatively high concentration of organic material. The possibility that high concentrations of halomethanes might be formed has caused some concern among regulatory agencies over the impact of breakpoint chlorination on downstream water uses, including drinking water supply.

To provide data on the potential problems involved in halomethane formation during breakpoint chlorination of wastewater, a continuous-flow pilot plant project was conducted for a period of 9 weeks. The major objectives were to monitor the production of six volatile halogenated organic compounds during breakpoint chlorination of wastewater and to determine the removal efficiency of activated carbon with regard to these compounds. This report describes the facilities used for the project and summarizes the results obtained.

SECTION 2

CONCLUSIONS

After secondary treatment by a trickling filter system and tertiary treatment by lime clarification and filtration, municipal wastewater from a City of Cincinnati interceptor sewer contained small but measurable quantities of chloroform. The other five volatile halogenated organic compounds were detected less than half the time.

Breakpoint chlorination of the tertiary filter effluent caused the formation of 43 µg $CHCl_3$/l and 4.4 µg $BrCHCl_2$/l (median values). The other four compounds were formed infrequently and/or in small amounts.

No correlations were observed between the amount of chloroform formed and any other measured parameter.

Breakpoint chlorination of the tertiary filter effluent increased the concentration of extractable organic chlorine in three sets of samples by an average of 11.0 µg/l.

Treatment of the tertiary filter effluent with a 10-min contact time, granular activated carbon column before breakpoint chlorination reduced the median values of $CHCl_3$ and $BrCHCl_2$ formed during chlorination to 12 µg/l and 2.5 µg/l, respectively. There was no net production of the other four compounds in this system.

The carbon lost its ability to reduce the formation of bromodichloromethane after treating approximately 4500 bed volumes of wastewater; the carbon continued to reduce the amount of chloroform produced up to the termination of the study (8400 bed volumes).

Carbon treatment reduced the amount of extractable organic chlorine formed during chlorination by an average of 8.1 µg/l in three sets of samples.

Batch chlorination test results with chlorine doses in the wastewater disinfection range showed little or no chloroform production over a period of 40 hr of contact time.

The service life of the 20-min contactor treating chlorinated tertiary filter effluent was much more than twice that of a 10-min contactor. The carbon utilization rate of the 20-min contactor treated as a single-stage

contactor was 200 g/cu m, compared to a utilization rate of 340 g/cu m for the 10-min contactor, with 5 µg $CHCl_3$/l in the effluent as the exhaustion criterion.

The capacity of the second-stage columns to remove chloroform was a precise function of the average influent concentration. The first-stage column removed $CHCl_3$ less efficiently than the second-stage column, presumably because more strongly adsorbed organics were preferentially adsorbed in the first stage; thereby reducing the competition for adsorption sites in the second stage.

The removal of chloroform by carbon was not affected by the presence of 12 mg/l of total residual chlorine.

SECTION 3

RECOMMENDATIONS

More detailed information on the formation of halogenated organics by chlorination of wastewater should be obtained for a broader range of compounds under closely controlled conditions. Identification and quantification of halogenated compounds formed during breakpoint chlorination would be of interest. Effects of physical and chemical factors on yield and rate of formation should be examined. Toxicity testing could be a valuable aid in determining the necessity of minimizing the release of halogenated organics to the aquatic environment.

Studies on optimization of trihalomethane and precursor removal by activated carbon should be undertaken, particularly with respect to drinking water treatment. The influence of contact time on carbon utilization rate should be carefully examined on a variety of waters. Contacting modes should be compared (multistaged series, countercurrent, parallel single stage). Batch equilibrium tests should be conducted for comparison with continuous-flow exhaustion data.

If the discharge of chloroform is to be limited in a system utilizing breakpoint chlorination and activated carbon, locating the chlorination reactor between stages of a two-stage system would be more desirable than locating it ahead of carbon treatment. This arrangement would take advantage of precursor removal in the first stage and chloroform removal and dechlorination in the second stage.

SECTION 4

BACKGROUND

AMMONIA IN WASTEWATER

Ammonia nitrogen is found in all municipal wastewaters. Human fecal matter contains organic nitrogen, some of which is converted to inorganic ammonia by natural biological decomposition. Likewise, the urea in urine is hydrolyzed to ammonia during the time of collection, transport and storage in a municipal system.

Ammonia nitrogen can exist in wastewater as the ion NH_4^+ or the dissolved gas NH_3. The equilibrium expression:

$$NH_3 + H^+ \longleftrightarrow NH_4^+ \qquad K = 5.0 \times 10^{-10} \text{ @ } 20^{\circ}C \qquad (1)$$

indicates that at neutral pH the ammonium ion is the predominant species. In this report the terms ammonia or ammonia nitrogen or NH_3-N will refer to the sum of the concentrations of NH_3 and NH_4^+ expressed as nitrogen.

The requirements for removal of ammonia from wastewater depend upon a number of factors. Nitrogen discharged to lakes, estuaries or bays can accelerate the eutrophication of such bodies of water. Ammonia nitrogen exerts a demand upon the oxygen resources of either standing or flowing bodies of water due to bacterial oxidation of ammonia to nitrite and nitrate. The stoichiometric requirement is 4.6 mg oxygen per mg ammonia oxidized. Other considerations, such as fish toxicity and impairment of disinfection efficiency could also result in a requirement for ammonia removal from wastewater.

AMMONIA REMOVAL

The most widely practiced method for reducing the concentration of ammonia in wastewater has been biological oxidation to nitrate (nitrification) in activated sludge or fixed film reactors. Nitrification can be followed by biological denitrification, wherein the nitrate is reduced by biological action to nitrogen gas. Nitrification can be used alone to control the problems of ammonia discharge, e.g., nitrogenous oxygen demand, ammonia toxicity, etc. However, nitrate nitrogen is still present to act as an algal stimulant. Thus, nitrification must be followed by denitrification to accomplish more or less complete removal of inorganic nitrogen.

In contrast to the biological mechanism of ammonia control which results in conversion of ammonia to nitrate, several physical-chemical processes are available that eliminate the ammonia nitrogen from the wastewater.

Air-stripping involves providing intimate contact of air with wastewater at pH > 11. Ammonia is in the form of dissolved gas at this pH and thus is available for transfer to the stripping air. This process can be accomplished in conventional cooling towers, but problems of scale formation on the packing and inefficient stripping and freezing in cold weather require special considerations. A modification of the process passes the ammonia laden exhaust air through an absorption tower where an acid solution absorbs the ammonia and eventually produces a fairly concentrated solution of ammonium salt with some commercial value. The air is continuously cycled through stripping and absorption towers in a closed system so that the CO_2 quickly disappears and calcium carbonate scale formation is eliminated.

Ammonia can also be removed from wastewater by ion exchange using an ammonium selective zeolite, clinoptilolite. Regenerant brine can be recovered and reused by stripping the ammonia at elevated pH. The closed stripping - adsorption system described above will be used at several full-scale installations to remove ammonia from the regenerant brine.

BREAKPOINT CHLORINATION FOR NITROGEN REMOVAL

Chlorine is a strong oxidant which, when added to wastewater in sufficient concentration, can oxidize inorganic ammonia to nitrogen gas. The chemistry of the process is still somewhat undefined and will be discussed only briefly here. Thorough discussions can be found in the literature (1-13).

Chlorine gas dissolves in water according to the hydrolysis reaction:

$$Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^- \qquad (2)$$

Hypochlorous acid (HOCl) dissociates to maintain an equilibrium with the hypochlorite ion:

$$HOCl \longleftrightarrow H^+ + OCl^- \quad K = 3.3\times10^{-8} \ @ \ 20°C \qquad (3)$$

Both HOCl and OCl^- are active forms of aqueous chlorine. In this report the sum of the concentrations of HOCl and OCl^- will be designated as "free" chlorine without regard to their proportions. Chlorination systems may use either gaseous chlorine or hypochlorite (commonly sodium hypochlorite); the resulting form of free chlorine depends upon the operating pH and temperature.

Aqueous chlorine reacts with ammonium ion to form a number of N-chloro compounds known as chloramines. Monochloramine (NH_2Cl) is usually formed if the pH is near neutral and the $Cl:NH_3$-N weight ratio is less than 5:1. At low pH or higher $Cl:NH_3$-N ratios, dichloramine ($NHCl_2$) can be formed

and under certain conditions (e.g., very high $Cl:NH_3$-N ratio) trichloramine or nitrogen trichloride (NCl_3) is produced. The total chloramine concentration is referred to as "combined" chlorine.

The concept of breakpoint chlorination (BPC) is illustrated in Figure 1, a theoretical breakpoint curve. As chlorine is added to a dilute solution of ammonia, the total chlorine residual increases at nearly the same rate as the chlorine addition up to a $Cl:NH_3$-N weight ratio of about 5:1. Then as more chlorine is added, the measured residual begins to decline until some point is reached at which the chlorine residual is at a minimum. Beyond this point the measured residual increases at the same rate as the applied chlorine. The minimum point is known as the breakpoint. Beyond the breakpoint the chlorine residual is nearly all "free" residual chlorine, while prior to reaching the breakpoint the measured total residual is "combined" residual or chloramines. The breakpoint is shown in Figure 1 as occurring at a $Cl:NH_3$-N weight ratio of 7.6:1. This is the minimum stoichiometric ratio possible via a reasonable sequence of reaction steps with N_2 as the only nitrogenous end product.

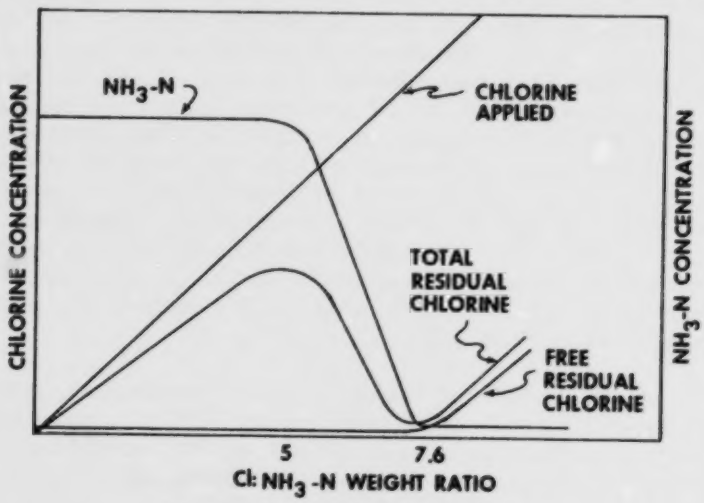


Figure 1. Breakpoint Curve.

The ammonia concentration begins to decline at about the 5:1 $Cl:NH_3$ ratio until ammonia is nearly completely absent at the breakpoint, It is generally accepted that as the applied chlorine increases from 0 up to the hump in the curve, monochloramine is being formed. The declining portion of the breakpoint curve is where dichloramine is formed and decomposes to yield nitrogen gas resulting in a decline of the ammonia nitrogen concentration. Stone (12) summarizes the stoichiometry of the most reasonable set of reactions leading to breakpoint with the following expression, modified slightly:

$$NH_4^+ + 1.5\ OCl^- \longrightarrow .5\ N_2 + 1.5\ H_2O + H^+ + 1.5\ Cl^- \qquad (4)$$

This accounts for the 7.6:1 minimum weight ratio (1.5:1 molar ratio) required for ammonia oxidation.

Other end products from the chlorination of ammonia, notably nitrate (NO_3) and nitrogen trichloride have been observed (1, 4, 10, 12). The production of these substances is to be avoided for a number of reasons. The formation of nitrogen trichloride results in a chlorine consumption of 15 mg for each mg of NCl_3-N produced. Nitrogen trichloride is a slightly soluble gas with an obnoxious odor. Its presence also contributes to the total nitrogen of the effluent, as it probably reverts to ammonia upon dechlorination (1). The formation of each mg of nitrate-N requires 20 mg of chlorine. The presence of nitrate also, of course, contributes to the total effluent nitrogen and should be minimized.

Equation 4 shows a net increase of one mole of hydrogen ions as one mole of ammonia is oxidized to N_2. In addition, if gaseous chlorine is used, the hydrolysis of sufficient chlorine to oxidize one mole of ammonia liberates three moles of hydrogen ion. These hydrogen ion additions could result in serious pH depression unless the wastewater alkalinity is sufficiently high or unless they are neutralized by addition of base. Palin (11) and Pressley et al. (4, 10) observed increased NCl_3 production at lower pH although Stone (12) and Saunier and Sellick (1) did not observe this effect. In any event, the pH of the reaction should be controlled as near neutral as possible. In order to neutralize the hydrogen ions produced, a source of hydroxide ions can be supplied in the form of, for example, lime or sodium hydroxide. Four equivalents of lime or sodium hydroxide translate to 1.05 or 1.50 parts of CaO and NaOH, respectively, needed for each part of chlorine added. In practice, the amount of lime or sodium hydroxide added would be controlled to maintain a constant pH in the reactor effluent. In a full-scale breakpoint study, Stone used 1.53 g NaOH/g Cl_2 using pH controlled sodium hydroxide feed (12).

Both the chlorine added and the alkalinity supplement contribute to a substantial increase in total dissolved solids (TDS) in the effluent. Gas chlorination with lime neutralization of all acidity would result in a TDS increase of 12 parts per part of ammonia destroyed, while the use of sodium hydroxide would result in a 15:1 increase in TDS (13). Sodium hypochlorite is purchased from chemical suppliers or manufactured on site in the form of a caustic solution. Thus the TDS and the pH adjustment chemical requirements would depend upon the caustic content of the solution fed.

Saunier and Sellick (1) conclude that the ammonia concentration reaches its lower limit in 60-90 seconds. Stone's data (12) on a full-scale pipeline reactor showed minimum ammonia concentration occurring at 100-200 seconds. Thus, small reaction vessels may be used for the breakpoint chlorination process.

During three months of operation of a 25 gpm (2.2 l/sec) BPC pilot plant with good process control, Pressley, et al. reduced the ammonia content of lime-clarified and filtered raw wastewater from 10.0 to 0.4 mg N/l (10). The chlorine to ammonia nitrogen weight ratio was 9:1 and the

pH was 7.1-7.3. The alkalinity requirement was 1.8 parts NaOH/part Cl_2. Little or no organic nitrogen removal was observed in the pilot operation, resulting in an effluent total nitrogen content of 2.5 mg N/1.

A large-scale demonstration of breakpoint chlorination was conducted at Rancho Cordova, California (12). A Cl:NH_3-N ratio of 10:1 was required to insure a controllable free residual chlorine (8 mg/1). In a series of experimental runs conducted in the pH range 7.0-8.0, the ammonia content of secondary effluent was reduced from a mean value of 17.7 mg N/1 to 0.55 mg N/1. Oxidation of NH_3-N to NO_3-N produced a mean value of 1.06 mg NO_3-N/1, with no apparent influence of pH in that narrow range. Organic nitrogen concentration was unchanged through the breakpoint process. All but 0-8% of the chlorine added could be accounted for in the oxidation of influent ammonia to N_2, NO_3 and NCl_3 (assuming all residual NH_3 was the product of dechlorination of NCl_3), the oxidation of NO_2 to NO_3 and the free residual remaining.

A variation of the breakpoint chlorination process using activated carbon has been examined by several investigators (14,15,16,17,18,19). During a pilot study at Owosso, Michigan, effluent from a chlorination system was treated with activated carbon for organic removal (14,15). It was observed there and subsequently confirmed by others that activated carbon can react with chloramines to form nitrogen gas and chloride. Thus, at chlorine dosages below the breakpoint, partial ammonia removal could be achieved if activated carbon followed the BPC system. Activated carbon following BPC also provides removal of the free-residual chlorine by reduction of the active chlorine species to chloride (20).

THE CHLORINATED ORGANICS PROBLEM

With the development of more sophisticated analytical tools came the awareness that a vast number of organic substances contaminate our nation's surface waters and can thus be found in drinking water supplies. In addition, it was observed both in the United States (21) and Europe (22) that some finished drinking waters contained trihalomethanes that were not found in the raw waters, indicating their formation during the process of chlorination.

A survey of the drinking water in 80 U. S. cities was made by EPA during 1975 (23). The concentration of six volatile halogenated organic compounds was determined by the gas chromatographic technique described by Bellar and Lichtenberg (24). Chloroform ($CHCl_3$) was found in the finished water of all 80 cities surveyed, ranging in concentration from barely detectable (>0.1 µg/1) to over 300 µg/1. Bromodichloromethane ($BrCHCl_2$), dibromochloromethane (Br_2CHCl), and bromoform ($CHBr_3$) were also found, although less frequently and in lower concentration. Carbon tetrachloride (CCl_4) and 1,2-dichloroethane ($C_2H_4Cl_2$) were detected in 88% and 68% of the finished waters, respectively, although there was no evidence of their formation during chlorination.

Chloroform has been named a suspected carcinogen, and its presence in drinking waters should be minimized. Stevens et al. (25) and Love et al. (26) have investigated the formation and removal of trihalomethanes in the treatment of surface waters with a variety of processes. Stevens et al. (25) show that applying chlorine after coagulation and settling rather than to raw water greatly reduced the amount of chloroform produced. Chlorination of solutions of humic acid gave similar results as chlorination of Ohio River water at similar levels of total organic carbon (TOC). Formation of trihalomethanes by chlorination of raw water, humic acid and acetone was enhanced at high pH, but acetone produced very little trihalomethane when chlorinated at neutral pH. The formation of chloroform in raw water increased with temperature. Very little trihalomethane was formed when combined chlorine (chloramine) was used rather than free chlorine. The formation of trihalomethane can proceed for days, until either the free chlorine residual or the precursor substance is exhausted.

Love et al. (26) examined the removal of trihalomethanes and trihalomethane formation potential (THMFP) by a variety of processes, including aeration, powdered and granular carbon, and ozonation. Trihalomethane formation potential was defined as the amount of trihalomethanes formed during contact with free chlorine for a specified time (several days) at a specified pH and temperature (27). It is an empirical designation that is analogous to the trihalomethane precursor concentration.

Variable results were obtained with granular activated carbon (GAC) (26). Treatment of chlorinated surface water with GAC in 5-min empty bed contact time pilot filters resulted in complete breakthrough of chloroform in 6 to 12 weeks. Brominated trihalomethanes were retained by the carbon for a longer period before breakthrough. After the GAC beds were exhausted, there was often desorption of trihalomethanes, indicating either true equilibrium (reversible adsorption) or displacement of trihalomethanes by more strongly sorbed substances. In one test, a 10-min contact time carbon contactor gave twice the service life as a 5-min contact time contactor. With an average influent chloroform concentration of 24 µg/l, the 10-min bed was completely exhausted for chloroform removal (0% removal) in 21 weeks. Assuming continuous operation, this amounted to an applied chloroform loading of 1.2 g $CHCl_3$/kg carbon at complete breakthrough.

A 5-min GAC adsorber removed chloroform formation potential for approximately 13 weeks, while a 10-min GAC adsorber was removing greater than 50% chloroform formation potential at the termination of the experiment at 30 weeks' service time. GAC was less effective in reducing the potential for formation of the bromodichloromethane and dibromochloromethane.

Morris, in a review of available literature, concluded that chlorination of natural waters ". . . does not lead to the formation of all sorts of chlorinated derivatives with any and all pollutants. Rather it proceeds by a limited number of well-defined reactions on a few specific types of organic structures" (28). It is well known chlorine reacts with phenols to produce chlorophenols, causing taste and odor problems (2,28). In wastewater, the number and concentration of organic compounds are such that it would be surprising if some chloro-organics were not formed during chlorination.

Jolley (29) found more than 60 chlorine-containing constituents in a series of experiments involving chlorination of primary and secondary effluents at relatively low (disinfection) doses. He estimated that approximately 1% of the chlorine added was associated with stable chlorine-containing organic compounds when chlorinating secondary effluent. Other investigators have also determined that reactions can indeed occur between added chlorine and organic constituents in sewage (30,31). Evans (32) found µg/l quantities of organic chlorine (extractable in 15% ethyl ether in hexane) were produced when breakpoint chlorinating a wastewater that had been treated with lime clarification, filtration, and activated carbon.

STUDY OBJECTIVES

Breakpoint chlorination is a candidate process for nitrogen removal in some circumstances. This study was instigated because of the very evident possibility of the formation of chlorinated organics when adding large doses of chlorine to wastewaters containing high concentrations of organic substances (relative to surface waters). The objective was to operate a pilot plant system simulating as nearly as possible a treatment train producing high quality (reuse quality) effluent and using breakpoint chlorination for nitrogen control. The magnitude of the chlorinated organics formation problem would be assessed together with the capability of activated carbon for removing the chlorinated organics and for preventing their formation. This was to be done on a continuous-flow pilot plant that would be subject to typical changes in wastewater characteristics. The process train consisted of:

1. Secondary treatment by trickling filter
2. Tertiary lime clarification
3. Neutralization
4. Granular media filtration (GMF)
5. Breakpoint chlorination (BPC)
6. Granular activated carbon adsorption (GAC)

Details of the treatment processes are provided later.

Because of the difficulty in measuring a large number of chloro-organics the trihalomethanes, $CHCl_3$, $BrCHCl_2$, Br_2CHCl, and $CHBr_3$ together with CCl_4 and $C_2H_4Cl_2$, were the halogenated organics measured routinely. There was a growing body of data on these compounds in relation to water treatment practice, and it would be possible to compare results of wastewater chlorination with water treatment. The analytical procedure was not overly time comsuming, therefore, the large number of samples would not impose an impossible burden on the analytical staff. To supplement the data provided by measurement of the six volatile halogenated organics (VHO), several sets of samples would be analyzed for extractable organic chlorine. Conventional pollution parameters would be measured to document the general efficiency of the system. Two chlorination systems would be installed, one after the GMF and before a two-stage GAC adsorber, and the other between stages of a second two-stage adsorber. A third adsorber without any chlorination would be run in parallel to the other two. With this arrangement, VHO removal, VHO precursor removal, general organics removal, and chlorine removal could be examined in relation to each other.

SECTION 5

DESCRIPTION OF FACILITIES

PROCESS EQUIPMENT

Raw wastewater was pumped continuously from a 72-inch (1.8 m) interceptor serving residential and industrial areas of Cincinnati. After primary clarification, the wastewater was directed to two parallel trickling filters, each 10 ft (3 m) diameter containing 8 ft (2.4 m) of 4 in (0.1 m) blast furnace slag as the attachment medium. The effluents from the trickling filters were directed to two 38-in (0.97 m) diameter secondary clarifiers. The flow rate through the primary-secondary system was 10 gpm (0.6 1/sec).

A schematic diagram showing the major elements of the tertiary clarification-filtration system is shown in Figure 2. Secondary effluent from the trickling filter system flowed by gravity to a collection sump. This sump contained a level detector which, at loss of flow, provided a signal to shut down all tertiary system pumps, feeders, etc., and, coupled with appropriate time-delays, to restart the system upon restoration of influent flow. Only one shift/day attention was normally provided; the automatic stop-start capability allowed the system to cope with periodic loss of flow due to pump station problems or occasional shut-down of the trickling filter system during odd hours.

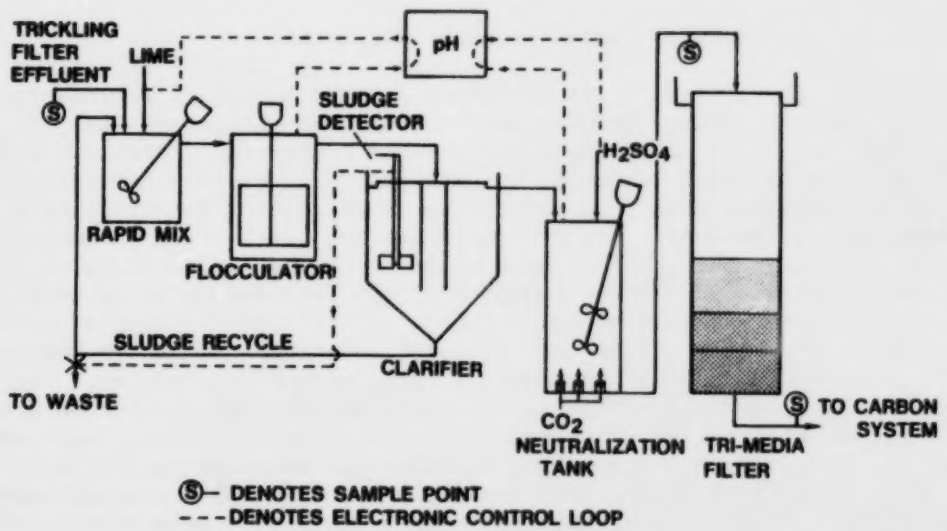


Figure 2. Flow diagram, tertiary lime clarification-filtration.

Secondary effluent was pumped at 5 gpm (0.3 l/sec) from the collection sump to the rapid mix unit by a Moyno pump (Robbins & Meyers, Inc., Springfield, Ohio). Flow was monitored by a 0.5 in (13 mm) magnetic flow meter (Fischer & Porter Co., Warminster, Pennsylvania) with remote indicator and recorder. The wastewater was mixed with an average dose of 414 mg $Ca(OH_2)$/l for a period of approximately 3 min in the baffled, 16 gal (0.06 cu m) rapid mix unit. Mixing energy was supplied by a 68 rpm turbine mixer. The lime dose was controlled automatically by a pH control system (Leeds & Northrup, North Wales, Pennsylvania). The pH was monitored by submersible probe in the flocculation unit downstream of the rapid mix tank. The probe was placed there in order to smooth out pH fluctuations caused by the pulsating action of the slurry pump and the automatic flushing of the pump head with tap water. The probe output was directed to a remote monitor and recorder and also to an electronic controller. The controller output regulated the lime slurry pump rate to maintain a constant pH of 11.2-11.5 in the clarification system. Lime slurry was prepared by adding preweighed 10 lb (4.5 kg) bags of $Ca(OH_2)$ to water in the amount of 1 bag/10 gal (1 bag/0.4 cu m). The slurry pump was a pH controlled diaphragm solution pump (Precision Control Products Corp., Meriden, Connecticut) that had been modified by replacing the pump head with that of a slurry pump head of the same manufacture. The slurry pump head was then equipped with a timed tap water flush to clear the head and ball checks of debris automatically. It was also necessary to acid clean the lime pump once a day with 50% HCl in order to dissolve scale formations that had accumulated on the pump head and check valves.

The flocculation tank was a 43 gal (0.16 cu m) baffled tank, providing a residence time of 9 min. Flocculation energy was provided by a 12 rpm mixer with two vertical 1-in wide (25 mm) paddles located 7.5 in (190 mm) from the center of rotation.

The flocculated wastewater entered the clarifier at a 6-in (150 mm) diameter center well which extended to a depth 60 in (1.5 m) below the water surface. The clarifier was 38 in (0.97 m) in diameter with a straight side depth of 56 in (1.4 m) and a 60° hopper bottom. Clarified wastewater flowed upward and over a peripheral effluent weir. Sludge settled to the hopper bottom where it was continuously pumped back to the rapid mix or to waste. The level of sludge in the clarifier was automatically maintained at or below a specified depth by a photoelectric sludge blanket level detector fabricated in our laboratory (Figure 3). When the sludge blanket level was below the elevation of the light source/photocell, no action was taken. When the sludge blanket rose to that point, the sludge blocked the light to the photocell. This break in photocell output triggered a control system which energized an electrically actuated ball valve to divert the sludge recycle stream to waste for a preset time interval. The clarification system could also be operated without continuously recycling sludge. Under this mode of operation the sludge level detector-controller turned on the sludge pump to waste for a preselected time. In either mode of operation, sludge wasting was followed by an automatic tap water flush of the sludge pipeline to prevent deposition in the line.

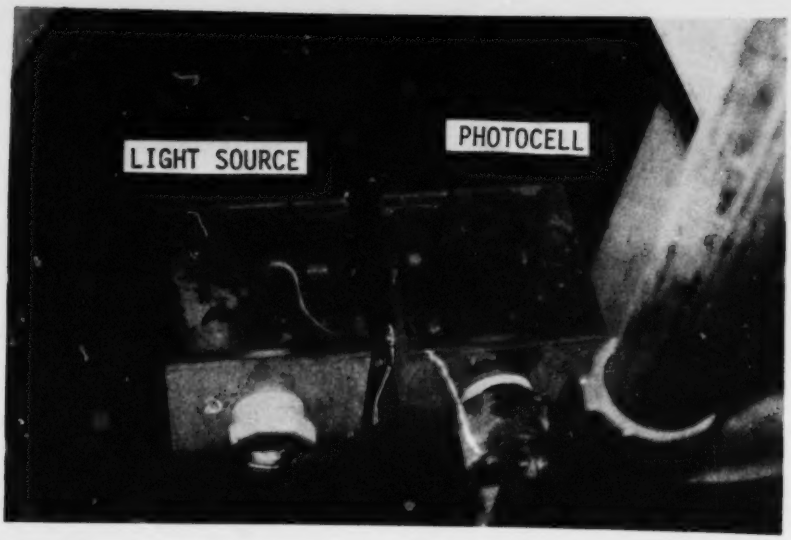


Figure 3. Sludge blanket level detector.

Effluent from the lime clarifier flowed by gravity to a rectangular tank for neutralization. The tank was 16 in (0.41 m) by 24 in (0.61 m) by 56 in (1.4 m) deep. The detention time was 16 min. The high pH lime clarifier effluent was neutralized to pH 7.0-7.2 by adding sulfuric acid and a manually controlled amount of carbon dioxide gas. The sulfuric acid addition was controlled by a Leeds & Northrup pH control system similar to that used to control the lime feed rate. Carbon dioxide was added to provide bicarbonate alkalinity (buffer capacity). This allowed much smoother neutralization pH control and provided buffer capacity required for downstream processes. A constant speed Moyno pump transferred neutralized effluent to the next process, gravity filtration. The transfer pump rate was slightly higher than the flow into the neutralization tank. A recycle line off the pump discharge line returned sufficient flow to the neutralization tank so that the outflow from the neutralization tank was paced to the inflow. The float operated valve that controlled the recycle flow also maintained the proper water level in the neutralization tank for efficient CO_2 dissolution.

The gravity filter was 11 in (0.3 m) square cross section. The media consisted of 3 in (80 mm) of 40x80 US mesh garnet sand, 9 in (230 mm) of 20x40 US mesh silica sand and 9 in (230 mm) of 10x20 US mesh anthracite filter media. After initial backwashing, the garnet sand layer became mixed with the silica sand layer and lost its identity. Flow was in a downward direction with gravity as the driving force. The flow rate through the filter was controlled at 3.3 gpm (0.21 l/sec) by three Moyno pumps on the effluent line. The resulting hydraulic loading was 3.9 gal/min/sq ft (9.5 m/hr). These pumps supplied filter effluent to the downstream processes. Any excess

filter influent overflowed the top of the 10 ft (3 m) high filter and was directed to an automatic sampler. The filter media support was a #80 US mesh stainless steel screen sandwiched between two PVC perforated plates supported by an open-grid false bottom.

The head loss in the filter operation was monitored by a piezometer-bubbler tube-pressure switch arrangement. When the filter clogged to the extent that the low pressure limit was reached, the monitor automatically shut down the transfer pump that supplied water to the filter and all downstream equipment. An alarm was sounded, signaling the high head loss shutdown condition. Backwash by an air-scour-water wash system was then initiated by the operator. After the water was drained to a level just above the top of the filter media, the bed was scrubbed by introducing air into the underdrain plenum. Two to three minutes of air scour at approximately 8 scfm/sq ft (150 m/hr) was followed by a five-minute water wash at approximately 90% expansion. After backwash was completed, the operator initiated filter and downstream process operation by means of a pushbutton on the filter pressure monitor panel. The filter supply pump started and when the wastewater above the filter was at the proper level, the filter effluent pumps and all downstream processes were turned on automatically.

A schematic diagram of the breakpoint chlorination (BPC) activated carbon systems is shown in Figure 4. Three activated carbon systems were operated in parallel. All were two-stage series expanded bed systems operating on filter effluent. In System 3, the filter effluent underwent BPC before application to the first stage carbon adsorber. In System 2, the BPC system was located between the first and second stage adsorbers. System 1 had no BPC and was used as a control.

Each activated carbon system contained 8 ft (2.4 m) (at repose) of Filtrasorb 400 (Calgon Corporation, Pittsburgh, Pennsylvania) granular activated carbon per stage for a total depth of 16 ft (4.9 m). The hydraulic application rate to each adsorber was 6 gal/min/sq ft (15 m/hr) for a resultant contact time of 10 min/stage (based on empty bed volume, carbon at repose). The rate of flow to each carbon system was controlled by the filter effluent pumps and monitored by rotometers. The diameter of each adsorber was 5.8 in (15 cm). The carbon was cleaned weekly by a separate air scour-upward flow water wash. The air scour rate was 8 cu ft/min/sq ft (150 m/hr), and the water backwash rate was 15 gal/min/sq ft (37 m/hr).

The breakpoint chlorination systems are illustrated in more detail in Figure 5. The major components were one automatic ammonia analyzer (Technicon Instruments Corporation, Tarrytown, New York) common to both systems, one chlorination control unit, two sodium hypochlorite pump controllers, two sodium hypochlorite pumps (Precision Control Products Corporation, Meriden, Connecticut), two in-line static mixers, two cylindrical glass reactors and an automatic chlorine analyzer (Technicon) measuring both total and free chlorine. The ammonia monitor continuously measured the concentration of ammonia nitrogen in the filter effluent. An electrical signal proportional to the ammonia concentration was transmitted to the chlorination control unit, a special unit designed and fabricated in-house. As finally used, the major function of the control unit was to convert the 0-5 VDC signal from the autoanalyzer to a 12-20 mA signal to be supplied to the sodium

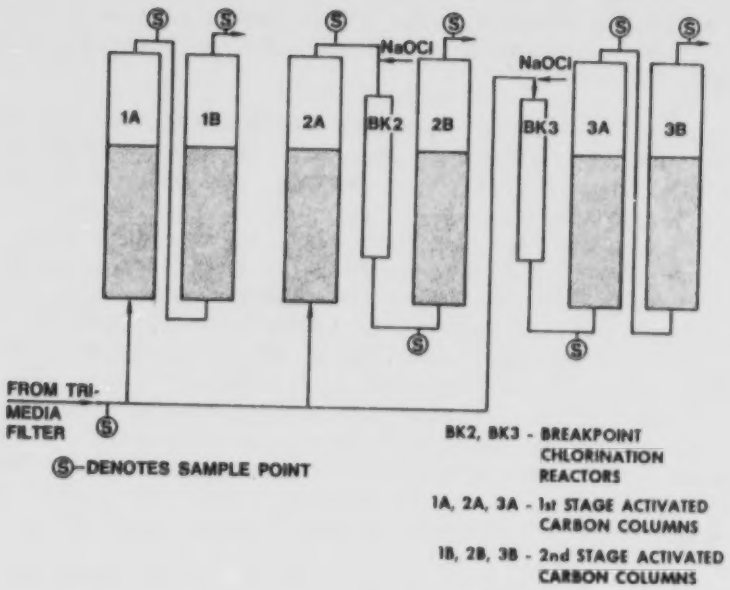


Figure 4. Carbon/chlorination system.

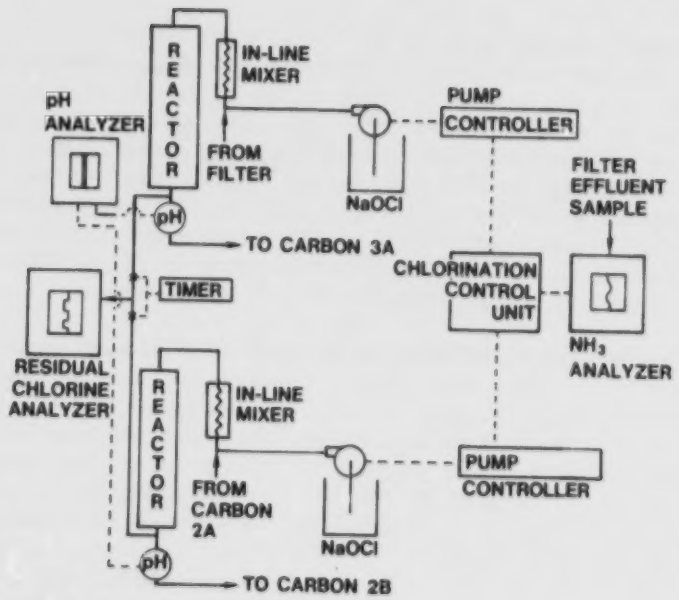


Figure 5. Breakpoint chlorination system.

hypochlorite feed pumps. The autoanalyzer signal could also be overridden by a manual input for use when standardizing the ammonia analyzer or correcting malfunctions.

Thus, the input signal to the sodium hypochlorite feed pump controllers was a function of the concentration of ammonia nitrogen in the filter effluent; this was the automatic feed forward control. The output:input ratio of each pump controller was adjusted manually according to the operator's observation of the free residual chlorine in each of the breakpoint reactor effluents; this was the manual feedback control.

Sodium hypochlorite was diluted with distilled water to a concentration of 7-9 g available chlorine per liter for use on the pilot system. The available chlorine concentration was checked daily. The sodium hypochlorite solution was pumped by the two diaphragm metering pumps through pulse eliminators, rotometers and back pressure regulators to mix with the breakpoint influents just upstream of two Kenics Static mixers (Kenics Corporation, Danvers, Massachusetts). Each chlorinated stream then entered a 3.8 in (95 mm) I.D., 60 in (1.5 m) long glass reactor with a detention time of 2.7 min. Sequenced samples of each reactor effluent were directed to the chlorine monitor, an autoanalyzer (Technicon) for measurement of free and total residual chlorine. The operator could then observe the state of the breakpoint chlorination process in each reactor and adjust the output:input ratios of sodium hypochlorite pump controllers to maintain the proper conditions. Additional information was available from the continuous recording of the pH of each reactor effluent. Reactor pH was controlled only by adjustment of the pH and alkalinity of the lime clarifier neutralization tank contents. When all systems were under control, the reactor effluents were at a pH of 7.0 ± 0.5.

A second residual chlorine analyzer accepted sequenced samples from the final effluent from carbon column 2 and from the first and second stage effluents from carbon column 3. The purpose of monitoring these streams for residual chlorine was to obtain data on the efficacy of activated carbon for removal of chlorine residual. A great deal of difficulty was encountered with this analyzer, and thus the amount of data obtained on this aspect of the system was minimal.

SAMPLING SYSTEMS

Effluents from the trickling filter, clarifier, neutralization tank, filter, breakpoint reactors and first and second stage carbon columns were sampled by the automatic sampling systems shown in Figures 6 and 7. The dipper samplers illustrated in Figure 6 were used to obtain automatic composite samples from all process streams after the filter. Small volumes of the process streams were directed continuously to the sample chambers to keep them full. The dippers rotated once each 15 min, collecting 8 ml aliquots and discharging them to their respective collection troughs, where they were drained to refrigerated sample bottles. The diverter samplers shown in Figure 7 were used for secondary effluent and neutralized lime clarifier effluent since suspended solids tended to settle in the dipper sample chambers.

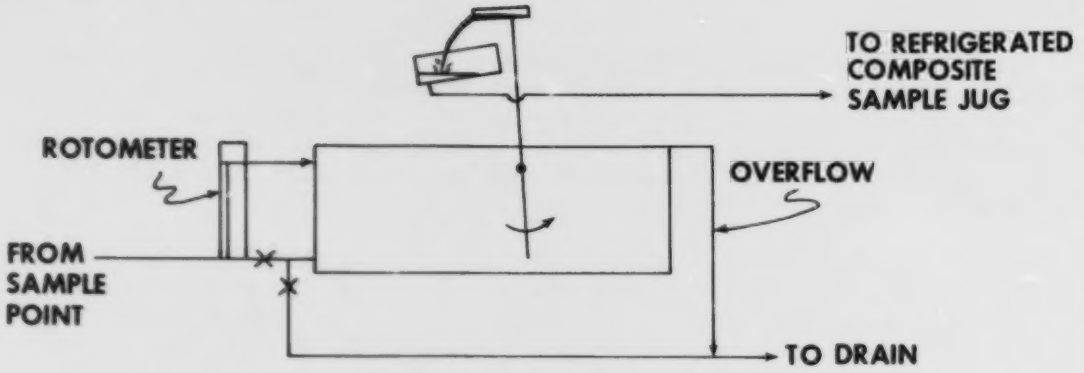


Figure 6. Dipper sampler.

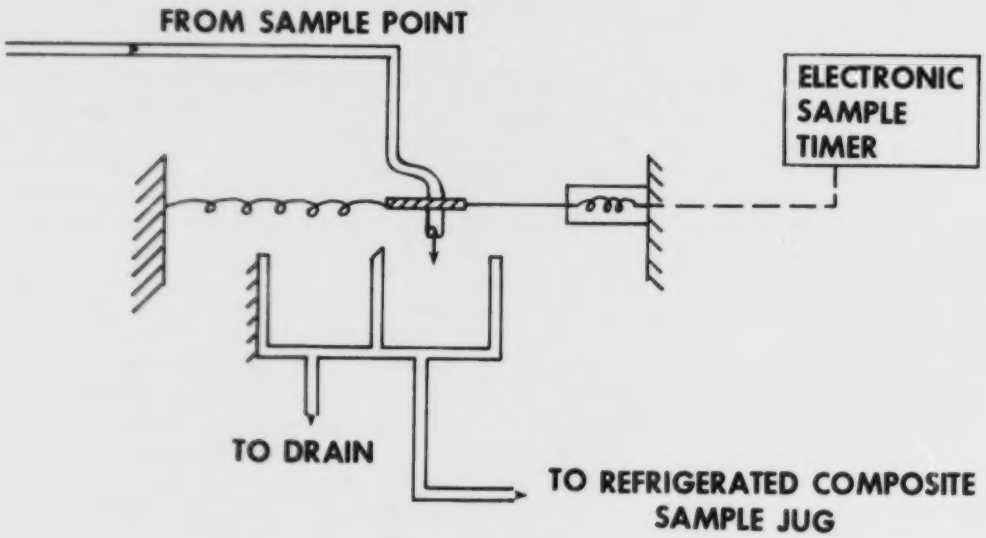


Figure 7. Diverter sampler in the sampling position.

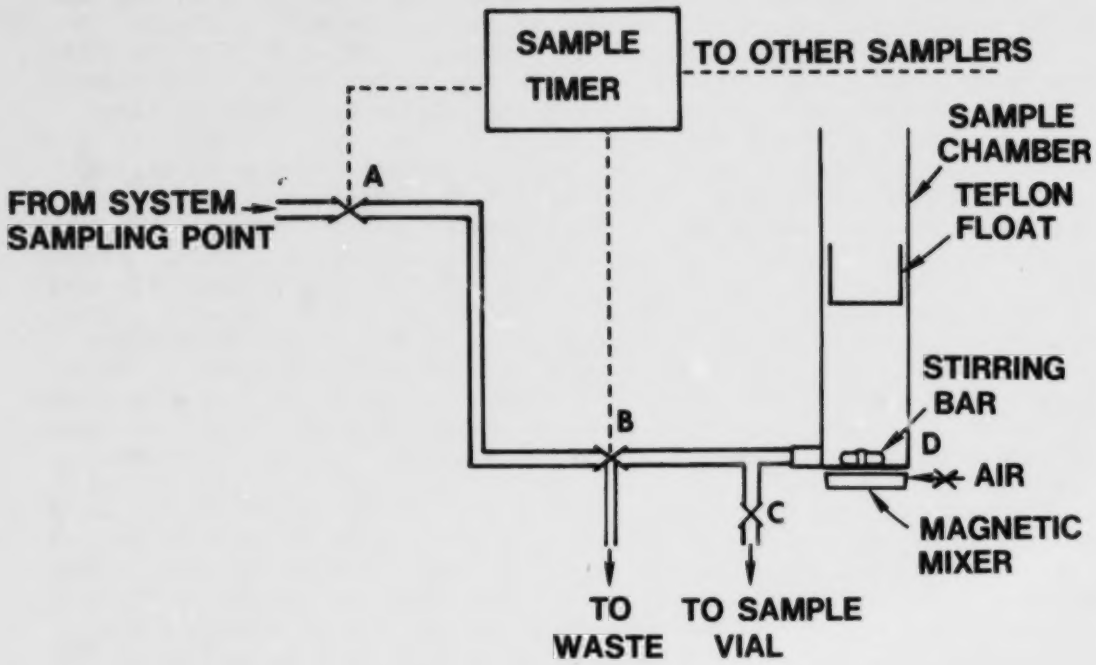
A special sampling apparatus was fabricated for use in obtaining composite samples for subsequent analysis of volatile organic compounds. A schematic of the apparatus is shown in Figure 8. Effluents from the filter, breakpoint reactors and first and second stage carbon columns were sampled with this system. An in-house designed and fabricated electronic timer, shown in Figure 9, opened the solenoid valve A to allow the sample to flush the sample line for a selected time interval through a three-way solenoid valve B to waste. The timer then energized the three-way valve for an instant so that the sample was diverted into the sample chamber. The sampling interval, the flush time and the sample impulse time were all adjustable to allow for the proper sample volume and to insure complete flushing of the sample line. The electronic timer operated a total of nine samplers. The composite sample chamber consisted of a 2-liter graduated cylinder equipped with a flat bottom and a glass tube inlet-outlet port. A Teflon float was machined to fit each sample chamber so that, as the sample volume increased, the float would ride up on the sample surface. This float apparatus permitted the collection of composite samples in closed containers and minimized the loss of volatile organics during the composite period. A few grains of sodium thiosulfate were added to each chamber at the beginning of each sample period to prevent further reaction of chlorine and precursors during the composite period. Each sample chamber contained a magnetic stirring bar which was used to mix the sample at the end of the composite period. An air driven magnetic mixer was located under the sample chamber to drive the stirring bar. The photograph in Figure 10 shows most of the components. The closed composite sampler is described in more detail elsewhere (33).

SYSTEM OPERATION

System operation and data collection commenced on June 3, 1976, and continued until August 9, 1976. This equipment ran 24 hours a day, 7 days a week with only minor periods of shutdown as a result of equipment malfunctions or interruptions in the supply of secondary effluent. Operator surveillance was provided eight hours per day during the week and four hours per day on weekends during the first half of the study. During the last five weeks, technicians were in attendance 20 hours per day on weekdays and 4 hours per day on weekends, resulting in much improved system operation.

The pH of the secondary effluent, flocculation tank, neutralization tank, and each breakpoint reactor were continuously recorded. There were high pH excursions (up to $\sim$ 11) in the breakpoint systems immediately upon startup of the chlorination units following a shutdown. These excursions were caused by the pulse eliminators unloading pressure upon cessation of process flow, and injecting excessive sodium hypochlorite into the reactor. When the system was restarted, that excess sodium hypochlorite resulted in higher than normal pH (and high free chlorine) exiting the reactors for a period of approximately 5-10 minutes.

The ammonia analyzer functioned very well with very little attention. The baseline and a standard were checked daily and very little drift was observed. The only problem in the use of the instrument was the time required to pump the sample from the process stream through the various



VALVE	TYPE	FUNCTION
A	2-WAY SOLENOID	DIRECT SAMPLE TO VALVE B
B	3-WAY SOLENOID	DIRECT SAMPLE TO CHAMBER
C	MANUAL TOGGLE	TRANSFER COMPOSITE SAMPLE TO VIAL & DRAIN REMAINDER
D	MANUAL NEEDLE	CONTROL MIXER SPEED

Figure 8. Automatic composite sampler for volatile halogenated organics.

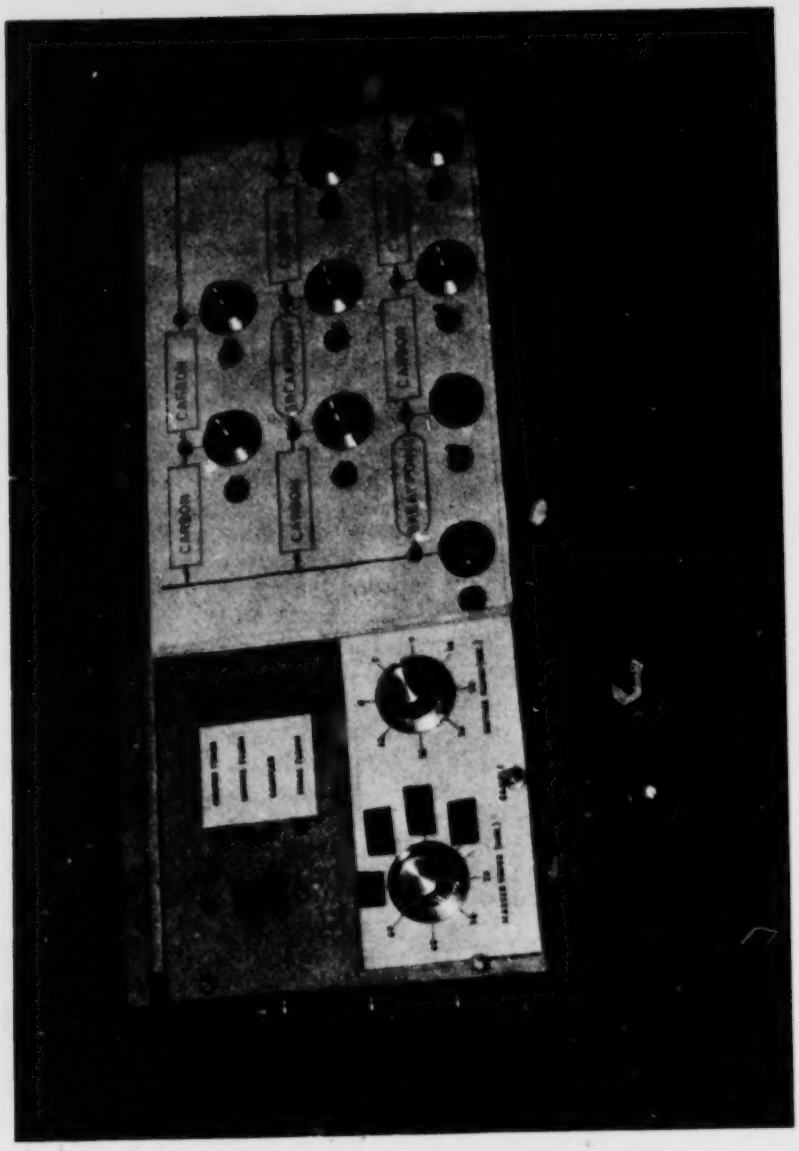


Figure 9. VHO sample programmer.

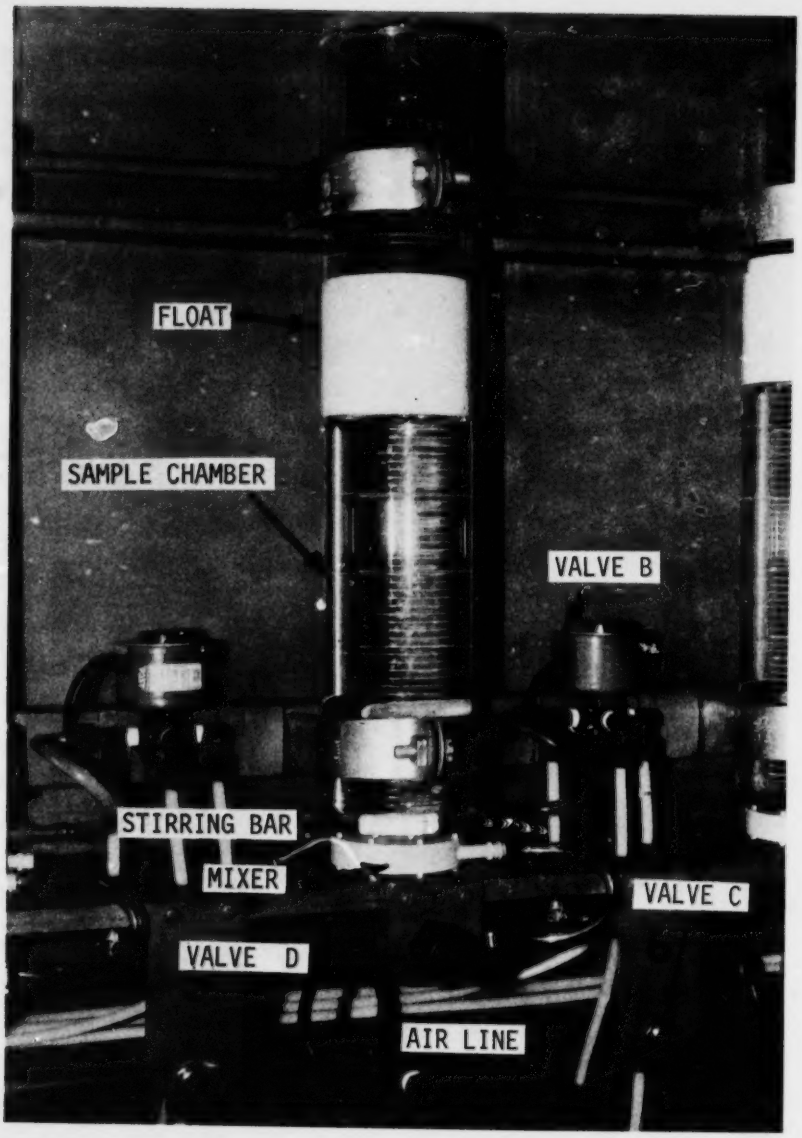


Figure 10. VHO sampler.

mixing coils and heating bath to the colorimeter. This resulted in a lag time of 15 minutes between a change in the ammonia concentration of the filter effluent and a corresponding change in the analyzer output - hence sodium hypochlorite feed rate. The normal diurnal variation of the wastewater resulted in a rather sharp increase in ammonia concentration of the filter effluent beginning early afternoon and ending in the early evening. This increase ranged from 1 mg/l/hr to as much as 6 mg/l/hr. This presented difficulties in maintaining breakpoint conditions. Although the influent ammonia increase could usually be accommodated by careful operator attention, there were occasions when the breakpoint was not reached. These occasions were indicated by high total chlorine residual but no free chlorine residual in the BPC reactor effluents.

The residual chlorine analyzers were usually reliable in indicating whether sufficient chlorine was being fed to reach the breakpoint. This was evident when the recorder trace of free and total chlorine residual were parallel, with total chlorine about 2-4 mg/l higher than free chlorine. At a dosage less than that required for breakpoint, the free chlorine trace was a straight line at or near zero, while the total chlorine read high, depending upon the actual chlorine to ammonia ratio being fed. There was usually 1-5 mg/l baseline drift in 24 hours.

Composite samples were taken from the refrigerated sample jugs three times per week, acidified, and placed into various containers for transfer to the analytical service laboratory. All operating data were summarized on the basis of each sample period,e.g., residual chlorine and ammonia nitrogen values were averaged over the operating time for each sample period. Lime and acid dosages were calculated from volume measurements and specified feedstock concentrations. Carbon dioxide feed rate was estimated from the rotometer readings. Sodium hypochlorite feed rates were determined by volume measurements and expressed as available chlorine. The chlorine concentration in each sodium hypochlorite stock tank was measured daily by the starch-iodine method.

At the end of the composite period, the contents of each of the closed composite samples were mixed with the stirring bars for a short period of time to assure that a representative sample would be withdrawn. Then valve "C" (Figure 8) was opened manually to allow the contents of the chamber to flow into the bottom of a 20 ml serum vial. The vial contents were displaced several times to minimize air contact and a convex meniscus was left at the top. The vials were then sealed with a Teflon disc held in place by a crimped aluminum cap. After the samples were transferred to the sealed vials, the remaining contents of the sample chambers were drained, and the floats were lifted out. The sample chambers were rinsed with distilled water, if necessary, and a few grains of sodium thiosulfate were placed in each chamber for dechlorination of the next composite sample. The floats were then reinserted, and the sampler was ready for another composite period.

SECTION 6

ANALYTICAL METHODS

LABORATORY ANALYSES

Composite samples were submitted to the Analytical Service Laboratory for analysis on Monday, Wednesday and Friday of each week. Total organic carbon (TOC) was measured on a Beckman Carbon Analyzer (Beckman Instruments, Inc., Fullerton, California) (34). Soluble organic carbon (SOC) was determined by filtering the samples through a 0.45×10^{-3} mm pore size membrane filter prior to analysis by the carbon analyzer. The TOC procedure removes carbonate interference by purging with nitrogen at pH 2. Thus, some volatile organic substances can be lost. Suspended solids and total dissolved solids (TDS) were determined by the procedures in Standard Methods (34).

The automated procedure described by Kamphake et al. was used to measure nitrite and nitrate concentrations (35). Ammonia nitrogen was determined by an automated phenate method (36,37). Total Kjeldahl nitrogen (TKN) was determined by manual digestion (34) followed by determination of the resulting ammonia by the automated phenate procedure.

The procedure of Bellar and Lichtenberg was used to measure the six volatile halogenated organic compounds (24,38,39). The volatile substances were purged from the sample with helium and collected on an adsorbent trap (Tenax). The trapped organics were then introduced into a gas chromatographic column (1.8 m x 4 mm glass column packed with 60/80 mesh Tenax) by helium purging at elevated temperature. The gas chromatograph was equipped with an electrolytic conductivity detector operated in the halide mode. Ammonia interference was overcome by acidifying the samples before purging to avoid ammonia volatilization. Peaks obtained as the output of the detector were identified by comparison with retention times of known standards. Concentrations were determined by comparison of peak heights with a standard curve.

A measure of the precision and accuracy of the analyses was obtained in the following way. A sample of breakpoint chlorinated, lime-treated secondary effluent was analyzed in replicate seven times. Another portion of the same sample was spiked with 10 µg/l each of the six VHO's, except bromodichloromethane which was added at 20 µg/l. At the time this test was conducted, the peaks of 1,2-dichloroethane and carbon tetrachloride could not be resolved. The peak at this retention time was arbitrarily assigned to 1,2-dichloroethane. The procedure was modified later to permit differentiation of the two compounds. The results of the evaluation of the method are

shown in Table 1. Both precision and accuracy were good. Recovery of the combined 1,2-dichloroethane/carbon tetrachloride was somewhat low since a single peak representing two compounds with differing instrument responses was measured.

Three sets of samples were analyzed for extractable organic chlorine. The method used was described by Evans (32). Each sample was extracted with a 15% solution of ethyl ether in hexane, the extracts were desiccated with sodium sulfate and the volume reduced to a few ml. The determination of organic chlorine was made with a Dohrmann Microcoulometer (Dohrmann, Division of Envirotech, Santa Clara, California). The instrument employs a microcoulometric halide detection cell in conjunction with a combustion furnace. In the determination of chlorine containing compounds, the sample is burned in the combustion zone at about 800°C in excess oxygen. Organic chlorine compounds are converted to gaseous hydrogen chloride which is measured by coulometric titration.

PILOT PLANT ANALYTICAL METHODS

The ammonia nitrogen in the filter effluent was continuously determined by a Technicon Monitor IV autoanalyzer. The method was the same as that used for the laboratory analysis. Free and total available chlorine residuals were continuously determined by a dual Technicon I system with a two-pen recorder. A modification of Palin's method (40), using diethyl-p-phenylenediamine indicator was developed (36). The analyzers were standardized at least once a day using the starch-iodine method (34). The operation of the chlorine analyzer was occasionally checked by feeding a solution of sodium hypochlorite to a buffered 5 mg N/l ammonia standard, while simultaneously measuring the total and free chlorine residuals. If the monitor were functioning properly, it would trace a typical breakpoint curve.

The concentration of chlorine in the sodium hypochlorite feed solution was determined daily by the starch-iodine method. Pilot plant staff measured composite sample alkalinity and turbidity; alkalinity was measured by titration with standard acid to pH 4.5 and turbidity with a Hach 2100 Turbidimeter (Hach Chemical Company, Ames, Iowa). All pilot plant continuous pH monitors were checked against the bench-top meter daily for evidence of drift. Occasional cleaning of the lime treatment and recarbonation pH probes prevented any serious difficulties in response time.

TABLE 1 - PRECISION AND ACCURACY OF VOLATILE HALOGENATED ORGANICS ANALYSIS*

	$CHCl_3$		$BrCHCl_2$		Br_2CHCl		$CHBr_3$		$ClCH_2$-CH_2Cl + CCl_4 +	
	Replicate Sample	10 µg/l Spike	Replicate Sample	20 µg/l Spike	Replicate Sample	10 µg/l Spike	Replicate Sample	10 µg/l Spike	Replicate Sample	10 µg/l Spike
	45	50	1.6	22	N†	10	N	10	N	16
	47	58	1.3	22	N	10	N	11	N	18
	41	57	1.6	24	N	10	N	10	N	17
	45	54	1.3	22	N	10	N	10	N	17
	42	55	1.4	22	N	11	N	12	N	17
	40	48	1.5	22	N	12	N	13	N	15
	44	52	1.3	22	N	12	N	13	N	15
Avg.	43.4	53.4	1.43	22.3	N	10.7	N	11.3	N	16.4
S.D.	2.5	3.6	0.138	0.76	-	0.95	-	1.4	-	1.1
Recovery	-	100%	-	104%	-	107%	-	113%	-	82%

* All values - µg/l
\+ Spiked with 10 µg/l each - see explanation in text.
† N - No peak observed.

SECTION 7

RESULTS AND DISCUSSION

GENERAL PROCESS PERFORMANCE

The lime clarification-filtration system received secondary effluent from the trickling filter system. The pH of the lime clarification was held in the range 11.2-11.5, depending upon observations of effluent clarity. The average lime dosage requirement was 414 mg $Ca(OH)_2$/l. Neutralization was achieved with a sulfuric acid dosage of 1.2 meq/l and sufficient CO_2 to bring the alkalinity to approximately 100 mg/l as $CaCO_3$. The neutralization pH set point was normally maintained at 7.0-7.2 in order that the pH of the breakpoint reaction would be 7.0.

Table 2 shows the effect of the lime clarification-filtration system on the trickling filter system effluent. The TOC was reduced by 63% with a 20% reduction in SOC. The secondary effluent was fairly low in nitrogen and was partially nitrified. The increase in ammonia and TKN which occurred during the lime clarification and neutralization step was the result of deliberate addition of 3-5 mg N/l of ammonium sulfate to the neutralization tank. This was done to ensure that the ammonia content of the waste would remain above the lower limit of control for the breakpoint chlorination control system.

Table 2 shows a decline in nitrate-nitrogen concentration from 5.5 mg/l to 2.3 mg/l in the filter effluent. This decline was probably the result of the proliferation of biological slimes which developed in the neutralization tank, in the pipeline leading to the filter and, possibly, within the filter itself. The slime development could also have resulted in some SOC removal. The growths became so profuse that sloughing biomass caused severe filter head loss buildup and very short filter runs. Therefore, twice a week, while the system was shut down, the neutralization tank, the transfer pipeline and the filter were chlorinated. This was done carefully to prevent contamination of any sample or contact of the highly chlorinated neutralization tank contents with the activated carbon.

The suspended solids and turbidity removal were what might be expected from a system of this kind. There was a net increase in TDS and a net decrease in alkalinity as a result of the lime addition and neutralization.

Table 3 shows the operating conditions of the breakpoint chlorination systems. As seen in Figure 4, reactor 2 was located between carbon contactors 2A and 2B. Reactor 3 treated filter effluent and discharged to carbon contactor 3A. The ammonia concentrations shown in Table 3 are

derived from the laboratory analyses of the composite samples. All other data shown here were taken from pilot plant operating records.

TABLE 2 - PERFORMANCE OF LIME CLARIFICATION-FILTRATION OF SECONDARY EFFLUENT

Parameter	Average Concentration S*	L+	F†
TOC	32.9	13.8	12.1
SOC	13.8	10.8	10.2
TKN §	7.7	9.5	9.5
NH_3-N §	3.8	7.7	7.5
NO_2-N	0.5	1.1	1.2
NO_3-N	5.5	2.6	2.3
SS	35	6	2
TDS	504	649	648
Turbidity, JTU	26	2.4	1.9
Alkalinity as $CaCO_3$	152	103	107

* S - Secondary effluent.
\+ L - Neutralized lime clarifier effluent.
† F - Granular media filter effluent.
§ - 3-5 mg NH_3-N/l added to clarifier effluent

TABLE 3 - AVERAGE OPERATING CONDITIONS OF BREAKPOINT CHLORINATION SYSTEMS

	Breakpoint system 2	3
Location	Mid-carbon	Pre-carbon
Influent NH_3, mg N/l	8.4	7.5
Chlorine Dose, mgl/	71	83
Cl:N ratio	8.4	11.1
Total Residual Chlorine, mg/l	12.1	13.1
Free Residual Chlorine, mg/l	8.5	8.3

Influent and effluent ammonia concentrations and chlorine to ammonia nitrogen ratios for the two breakpoint systems are shown in Figure 11 and Figure 12. Figure 13 illustrates the breakpoint reactor chlorine residuals averaged over each sample period. The nitrogen data is summarized in Table 4. The influent to System 2 was slightly higher in ammonia concentration than the System 3 influent. This could have been the result of hydrolysis of organic nitrogen within the first stage carbon since the organic nitrogen in System 2 influent averaged about 1.3 mg/l less than that of System 3 influent.

TABLE 4 - NITROGEN REMOVAL BY BREAKPOINT CHLORINATION
(Average Values)

	Breakpoint system			
	2		3	
	Influent	Effluent	Influent	Effluent
NH_3, mg N/l	8.4	0.3	7.5	0.3
NO_2, mg N/l	0.2	0.1	1.2	0.1
NO_3, mg N/l	1.6	1.0	2.3	1.6
TKN, mg N/l	9.1	1.3	9.5	1.9

The pilot system was not designed to study the breakpoint chlorination process as such. Possible nitrogen transformations within the sampling system and the nature of the operation (widely variable influent concentrations, occasional loss of breakpoint, periods of unattended operation) limit the interpretation of the nitrogen data. For example, both breakpoint systems showed some removal of nitrate ion. This is most certainly erroneous since breakpoint chlorination has been shown to produce nitrates, not destroy them. Because the objective of this project was to document the production and removal of halogenated organics by the processes in question, no attempts were made to reconcile the nitrogen data. Investigations which were designed to provide data on the nitrogen and chlorine transformations during the breakpoint chlorination of wastewater have been conducted elsewhere (4).

The residual chlorine plots are indicators of how well the systems were controlled during a given sample period, the greater divergence of the free and total chlorine residual values indicating longer periods out of control. System 2 was generally easier to control because the lag time of the ammonia monitor approximately corresponded to the total detention time in the carbon column, so that the sensor and the control element were functioning on the same slug of wastewater. In System 3 the control element responded to

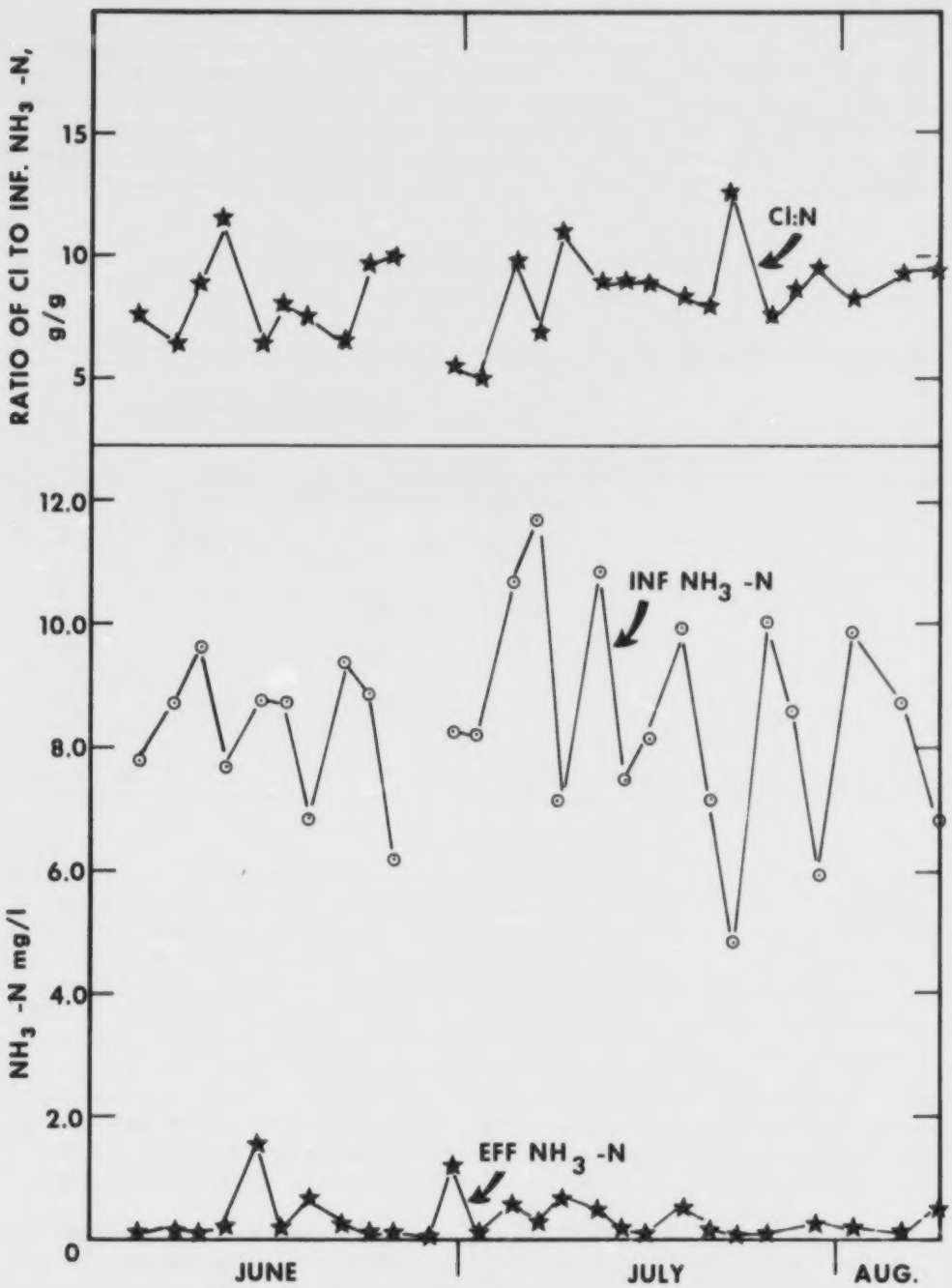


Figure 11. Ammonia removal - system 2

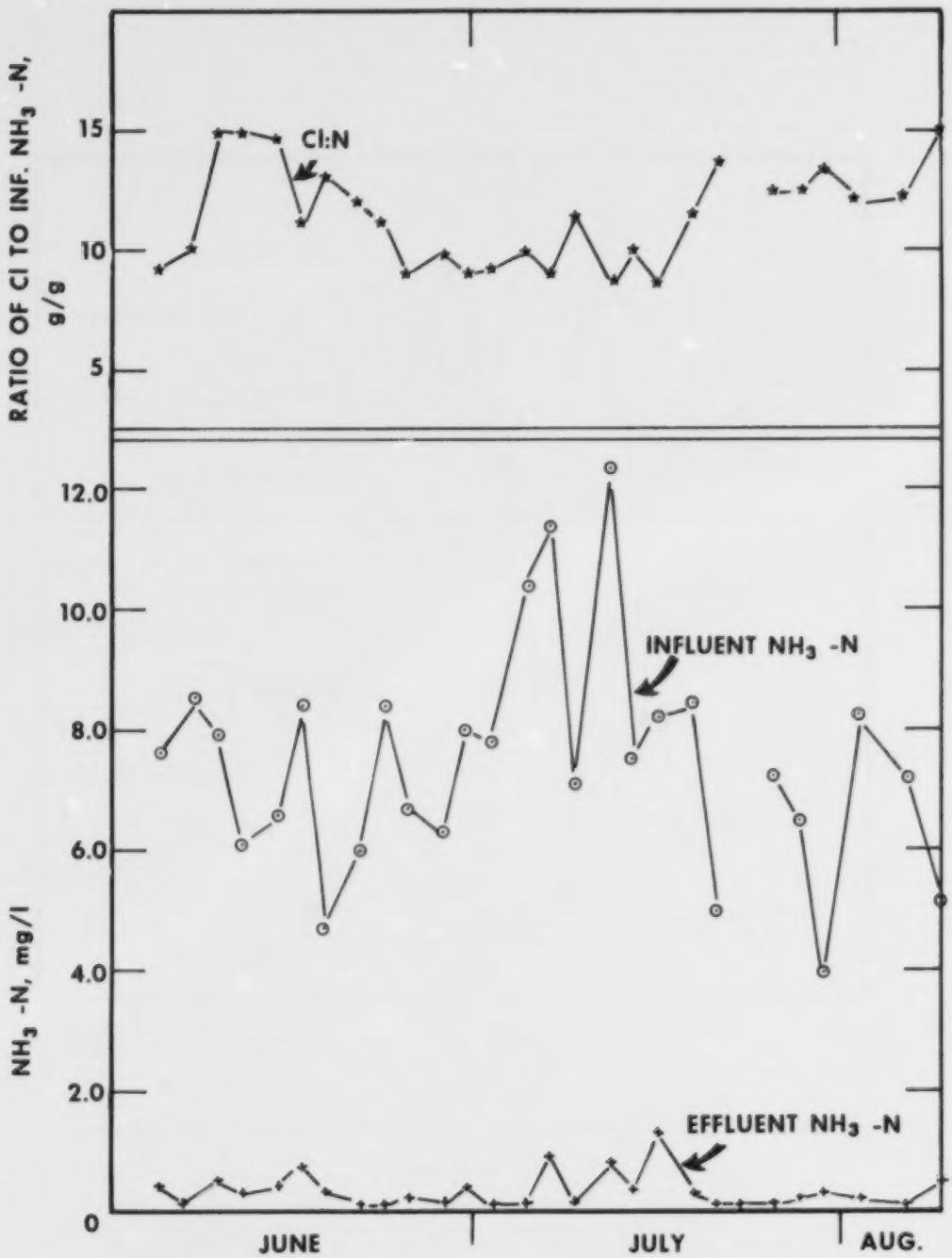


Figure 12. Ammonia removal - system 3.

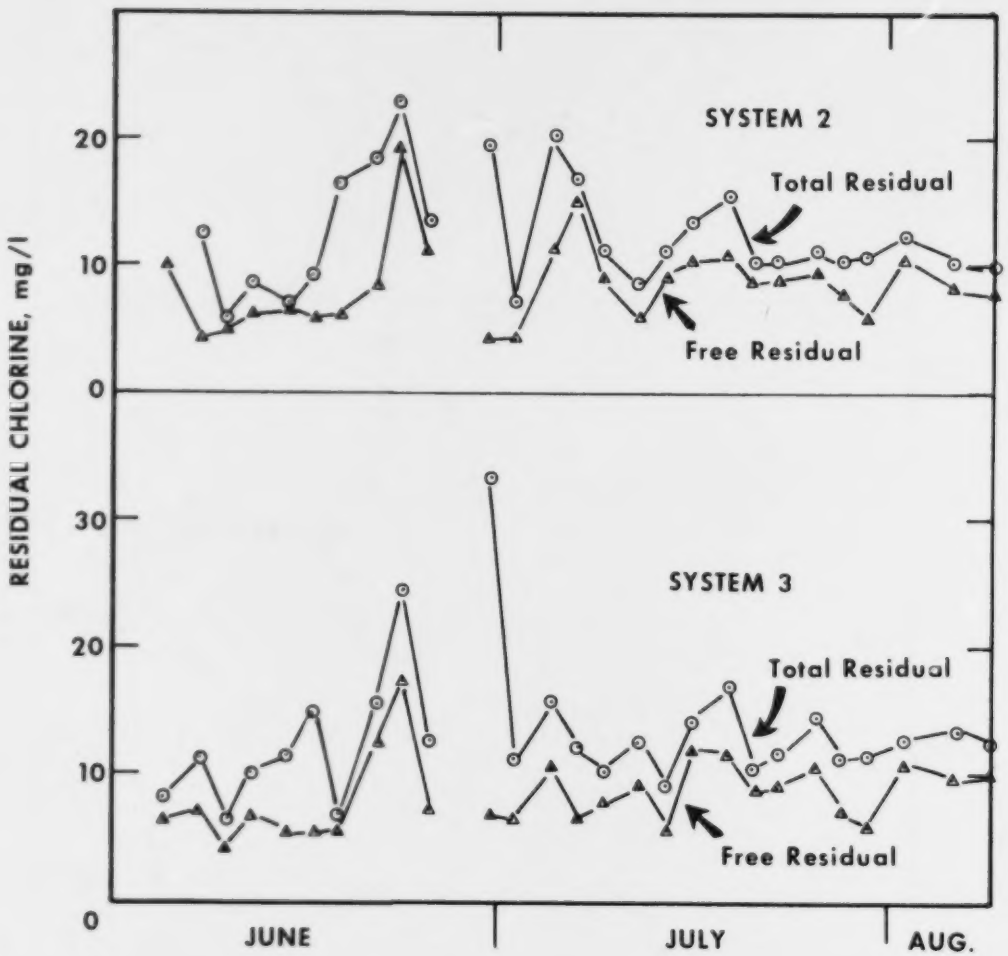


Figure 13. Residual chlorine after breakpoint chlorination.

changes in ammonia concentration 15 minutes after the changes occurred, making control more difficult and probably resulting in part in the higher Cl:N ratio required.

Table 5 shows the quality of the final effluents from the three carbon systems, with the filter effluent characteristics repeated for comparison. Removal of organic carbon by the three systems shows little difference on an average basis with average TOC of approximately 5 mg/l in the final effluent from each carbon system. The removal of soluble organic carbon by the GAC systems was quite erratic and showed no definable pattern of breakthrough, other than the presence of relatively high concentrations of SOC near the end of the study, shown in Figure 14.

TABLE 5 - FINAL EFFLUENT CHARACTERISTICS*

	Effluent			
Parameter	Filter	1B	2B	3B
Chlorine Reactor Location	-	None	Mid-carbon	Pre-carbon
TOC	12.1	5.3	4.6	5.1
SOC	10.2	3.3	3.9	4.2
TKN	9.5	3.9	1.0	1.2
NH_3-N	7.5	3.4	0.3	0.5
NO_2-N	1.2	1.0	0.1	0.2
NO_3-N	2.3	6.2	2.0	1.9
SS	3	1	2	1
TDS	648	638	876	869
Turbidity	1.9	1.0	1.5	1.5
Alkalinity as $CaCO_3$	107	78	116	116

* All values mg/l except turbidity (JTU).

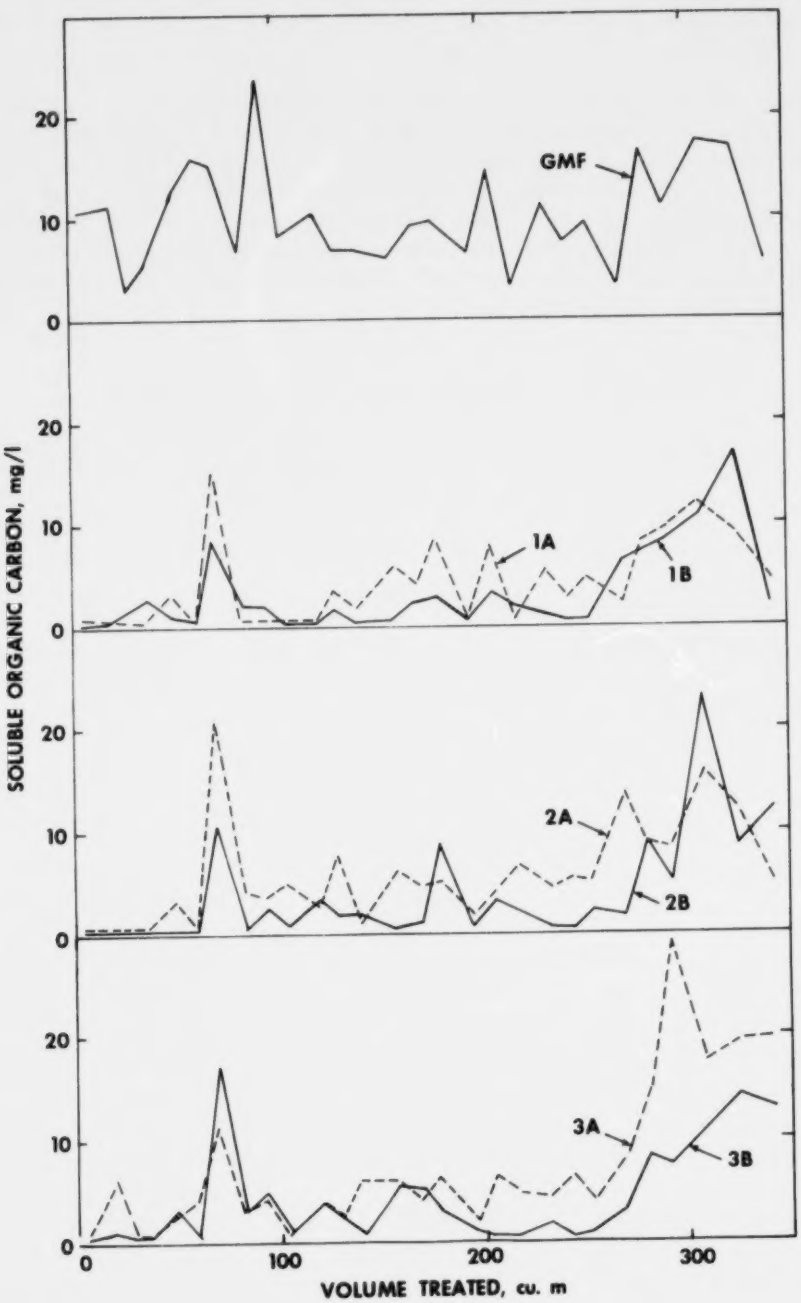


Figure 14. SOC removal by granular activated carbon.

The irregularity of the breakthrough data preclude use of organic carbon as a parameter in any rational comparison of the systems. The final effluent quality of all systems was excellent, with very low organic carbon and suspended solids. Again, the nitrate data are curious, showing an increase in nitrate concentration in the unchlorinated carbon system. This indicates the presence of nitrifying organisms, either in the carbon column itself or in the sampling system. However, the first stage effluent sample from carbon System 2 (2A) which should have been similar to the first stage effluent sample from carbon System 1 (1A) averaged 1.2 mg NO_3-N/1 as compared to 6.5 mg NO_3-N/1 in 1A. The reason for this difference has not been determined. The reduction in alkalinity in sample 1B tends to confirm the apparent nitrification of the ammonia. Alkalinity changes in the breakpoint systems were minimal, showing only a slight increase over the filter effluent. The increase in TDS was greater than expected, probably due to the somewhat undefined composition of the sodium hypochlorite feedstock.

FORMATION OF VOLATILE HALOGENATED ORGANICS

Breakpoint Chlorination of Granular Media Filter Effluent

Granular media filter effluent was chlorinated with an average dosage of 83 mg chlorine/1 for ammonia oxidation in System 3, with an average free chlorine residual of 8.3 mg/1. The volatile halogenated organic compounds, chloroform ($CHCl_3$), bromodichloromethane ($BrCHCl_2$), dibromochloromethane (Br_2CHCl), bromoform ($CHBr_3$), carbon tetrachloride (CCl_4), and 1,2,dichloroethane ($C_2H_4Cl_2$), were measured in composite samples of the influent and effluent of the breakpoint reactor. The results of these measurements are illustrated in the Appendix in Figure A1 through A5 and summarized in Tables 6 and 7. The minimum concentrations reported for all samples were: $BrCHCl_2$ and CCl_4 - 0.2 µg/1; $CHCl_3$, BrCHCl and $CHBr_3$ - 0.4 µg/1 and $C_2H_4Cl_2$ - 0.8 µg/1.

The predominant compound of those measured in the filter effluent was chloroform which was detected in all but four of the samples. The median value was 10 µg/1. Thus,through the sewer system, a trickling filter, clarifier overflows, and tertiary clarification-filtration, there remained a small but measurable residual of chloroform. Only two values were over 35 µg/1, one at 150 µg/1 and the second at 2400 µg/1. The source of the slug of 2400 µg/1 was never determined.

Bromodichloromethane and dibromochloromethane were detected in 11 of the 25 samples of the filter effluent, while bromoform was never detected. Carbon tetrachloride and 1,2 dichloroethane were detected infrequently but the maximum concentrations observed were 43 µg/1 and 44 µg/1, respectively.

Breakpoint chlorination of the filter effluent resulted in the reactor effluent concentrations shown in the Appendix in Figures A1 through A5, and summarized in Table 7. The amounts of each compound formed are shown in Figures A6 through A11 in the Appendix and summarized in Table 8. All samples of reactor effluent contained chloroform, with an increase in concentration over that of the filter effluent on all days except the two days when the filter effluent contained 150 µg/1 and 2400 µg/1. The median

TABLE 6 - CONCENTRATION OF HALOGENATED ORGANICS IN FILTER EFFLUENT*

Compound	Average	Median	Maximum	Minimum	% of days detected
$CHCl_3$	16+	10	2400	N†	84
$BrCHCl_2$	1.1	N	4.6	N	44
Br_2CHCl	2.1	N	9.7	N	44
$CHBr_3$	N	N	N	N	0
CCl_4	3.1	N	43	N	48
$C_2H_4Cl_2$	4.4	N	44	N	32

* All concentrations - µg/l.
\+ Maximum value of 2400 µg/l (July 2 slug) omitted from calculation of average.
† N - not detected.

TABLE 7 - CONCENTRATION OF HALOGENATED ORGANICS AFTER BREAKPOINT CHLORINATION OF FILTER EFFLUENT*

Compound	Average	Median	Maximum	Minimum	% of days detected
$CHCl_3$	80+	60	900	20	100
$BrCHCl_2$	6.9	5.3	23	N†	96
Br_2CHCl	4.3	3.9	17	N	65
$CHBr_3$	2.3	N	22	N	12
CCl_4	4.9	2.3	58	N	65
$C_2H_4Cl_2$	4.4	N	51	N	69

* All concentrations - µg/l.
\+ Maximum value of 900 µg/l (July 2 slug) omitted from calculation of average.
† N - not detected.

concentration of $CHCl_3$ in the chlorinated filter effluent was 60 µg/l with a range of 20 µg/l to 900 µg/l. The 900 µg/l value occurred on the day that the influent concentration was 2400 µg/l. Except for the two days when the effluent concentration was less than that of the influent, breakpoint chlorination caused the formation of from 17 µg/l to 335 µg/l of $CHCl_3$ in the filter effluent with an overall median value of 43 µg/l formed. This range of $CHCl_3$ concentration is similar to that found in the 80 city survey of finished drinking water supplies (23). However, the chlorine contact time in System 3 breakpoint reactor was only 3 min before dechlorination, while drinking water chlorination can go on for hours within a plant and days within a distribution system. A small number of batch chlorination tests were made after this study was completed (41). These will be discussed in more detail later. In two one-hour tests with frequent sampling the $CHCl_3$ concentrations after 3 min were 35% to 70% of those at 30 min, a common chlorine contact time. In a longer duration test the $CHCl_3$ formation potential at 48 hr was over 10 times the amount formed at 3 min. Therefore, the filter effluent undoubtedly contained sufficient precursor compounds to form greater quantities of chloroform than were observed, but the formation was limited by the short chlorine contact time. Because the chlorine-nitrogen reactions are complete in a fairly short time (1,12), there is no need for longer contact time for ammonia oxidation. Thus the time between chlorine addition and dechlorination can be dictated by other factors, such as the time necessary for stable control of chlorine feed rate, the time required for suitable destruction of pathogenic organisms, and the rate of formation of halogenated organics.

The bromodichloromethane concentration increased after breakpoint chlorination in all but one sample. It was formed in much lesser quantities than chloroform, with a median effluent concentration of 5 µg/l.

Dibromochloromethane was produced in the chlorination reactor less often and in lower concentration than $BrCHCl_2$ The carbon tetrachloride concentration was higher in the effluent than the influent over half the time. The average concentration increased from 3 to 5 µg/l, hardly a significant increase According to Morris (28) CCl_4 formation is unlikely. As is evident from Figures A9 and A11 and Table 8, there was essentially no production of bromoform and 1,2-dichloroethane.

Chloroform formation did not correlate with chlorine dose, chlorine residual, Cl:N ratio, effluent pH, or influent TOC, SOC or turbidity. Of these parameters only pH would be expected to correlate strongly, and the pH of this system varied little from sample period to sample period. Since chlorine residual and organic carbon are both several orders of magnitude greater than the chloroform produced, it would be surprising if these parameters did correlate. There is no reason to expect the chloroform precursor fraction of the TOC, for example, to remain constant in this wastewater. And since only a small fraction of the chloroform precursor was reacted, in the 4 min reaction time, the lack of correlation is to be expected.

For an indication of formation of non-volatile chlorinated organics, three sets of samples were assayed by the solvent extraction-microcoulometric procedure. The effect of breakpoint chlorination on the amount of these materials in the filter effluent is shown in Table 9. Quite low concentrations in the filter effluent were increased by 3-25 µg/l during the chlorination process. Thus, adding large amounts of chlorine to filter effluent did not result in large quantities of non-volatile chloro-organics being formed. This, again, could be a result of the short time of contact before dechlorination.

TABLE 8 - FORMATION OF HALOGENATED ORGANICS DURING BREAKPOINT CHLORINATION OF FILTER EFFLUENT*

Compound	Average+	Median+	Maximum	% of days formed
$CHCl_3$	64†	43	335	92
$BrCHCl_2$	5.7	4.4	22	96
Br_2CHCl	2.3	1.0	10	52
$CHBr_3$	2.4	0	22	12
CCl_4	1.9	0.5	15	52
$C_2H_4Cl_2$	0.2	0	15	16

* All concentrations - µg/l.
\+ Negative values included in average and median
† Data from July 2 (extremely high influent $CHCl_3$) omitted from calculation of average.

TABLE 9 - FORMATION OF SOLVENT-EXTRACTABLE ORGANIC CHLORINE COMPOUNDS DURING BREAKPOINT CHLORINATION OF FILTER EFFLUENTS*

Date	Reactor influent	Reactor effluent	Formed
6/25/76	3.7	6.5	2.8
7/9/76	6.6	11.5	4.9
8/9/76	2.3	27.7	25.4
Avg.	4.2	15.2	11.0

* All values µg organic chlorine/l.

Breakpoint Chlorination of First-Stage Carbon Effluent

The location of System 2 breakpoint chlorination reactor was after the first stage activated carbon column and before the second stage. Location of the chlorination system after the first stage of carbon treatment permitted comparison of the halogenated organics formed in System 2 with those of System 3, thus allowing inferences about the efficiency of the carbon for removing percursor organics.

Breakpoint System 2 operated with an average chlorine dose of 71 mg/l and an average free chlorine residual of 8.4 mg/l. Of the six volatile compounds assayed, only chloroform and bromodichloromethane were consistently higher after chlorination as shown in Table 10.

TABLE 10 - FORMATION OF HALOGENATED ORGANICS DURING BREAKPOINT CHLORINATION OF FIRST-STAGE CARBON EFFLUENT*

Compound	Average+	Median+	Maximum	% of days formed
$CHCl_3$	14	12	71	85
$BrCHCl_2$	2.9	2.5	10	73
Br_2CHCl	0.7	0	5.8	23
$CHBr_3$	0	0	0	0
CCl_4	0	0	5.8	38
$C_2H_4Cl_2$	0.4	0	5.7	12

* All concentrations - µg/l.
\+ Negative values are included in the average and median.

A comparison of Tables 10 and 8 shows that the median values of VHO formed in System 2 totaled 14.5 µg/l as compared to 49 µg/l, the total of the median values of the formation of compounds in System 3. The amount of chloroform produced by chlorinating after carbon treatment was only 25-30% of that formed by chlorinating before carbon treatment. Bromodichloromethane was formed in an amount of 50-60% of that formed in System 3. The observation that carbon was more effective in preventing the formation of $CHCl_3$ than $BrCHCl_2$ corroborates the findings of Love et al.(26) in the treatment of river water. Dibromochloromethane, carbon tetrachloride and 1,2-dichloroethane concentrations occasionally increased, but occasional decreases were also observed, resulting in little or no net formation. Bromoform was never detected in the influent or the effluent of System 2 chlorination reactor.

The time plot of $CHCl_3$ and $BrCHCl_2$ formation in System 2 breakpoint reactor shown in Figure 15 illustrates only slight, if any, increasing tendency with time on stream. However, when the differences between the amounts formed in System 2 and System 3 are examined, an indication of the precursor removal by carbon can be seen. Figures 16 and 17 are time plots of these differences. Figure 16 shows that the tendency to form less $CHCl_3$ during the first-stage carbon effluent chlorination had not been exhausted by the end of the study. Figure 17, on the other hand, shows that by mid-July, the difference in formation of $BrCHCl_2$ in the two systems was minimal. Therefore, after treating approximately 4500 bed volumes, the first stage of carbon treatment was no longer effective in reducing the formation of bromodichloromethane.

The extractable chlorinated organics data for System 2 breakpoint reactor are shown in Table 11. In all cases, lesser amounts of chloroorganics were formed by chlorination after carbon treatment than by chlorinating before. The August 9 sample indicated that the carbon was still removing precursor substances at the termination of the study, assuming all other factors equal. At that time, the first-stage carbon column was removing very little TOC, and thus the influents to the two chlorination reactors were nearly the same concentration. Although the carbon was exhausted in respect to TOC, it was still effective in reducing the amount of non-volatile chlorinated organics formed during breakpoint chlorination.

TABLE 11 - FORMATION OF SOLVENT-EXTRACTABLE ORGANIC CHLORINE COMPOUNDS DURING BREAKPOINT CHLORINATION OF FIRST-STAGE CARBON EFFLUENT*

Date	Influent	Effluent	Formed	Amount less than System 3
6/25/76	N+	2.0	2.0	0.8
7/9/76	1.8	3.1	1.3	3.6
8/9/76	1.3	6.7	5.4	20.0
Avg.	1.0	3.9	2.9	8.1

* All values µg organic chlorine/l.
\+ N - denotes not detected.

Batch Chlorination Tests

A limited number of batch chlorination tests were conducted after the pilot plant study had been terminated (41). The objectives were to obtain an indication of the effect of chlorine contact time on VHO formation and to examine the formation of VHO at chlorine dosages, less than breakpoint,

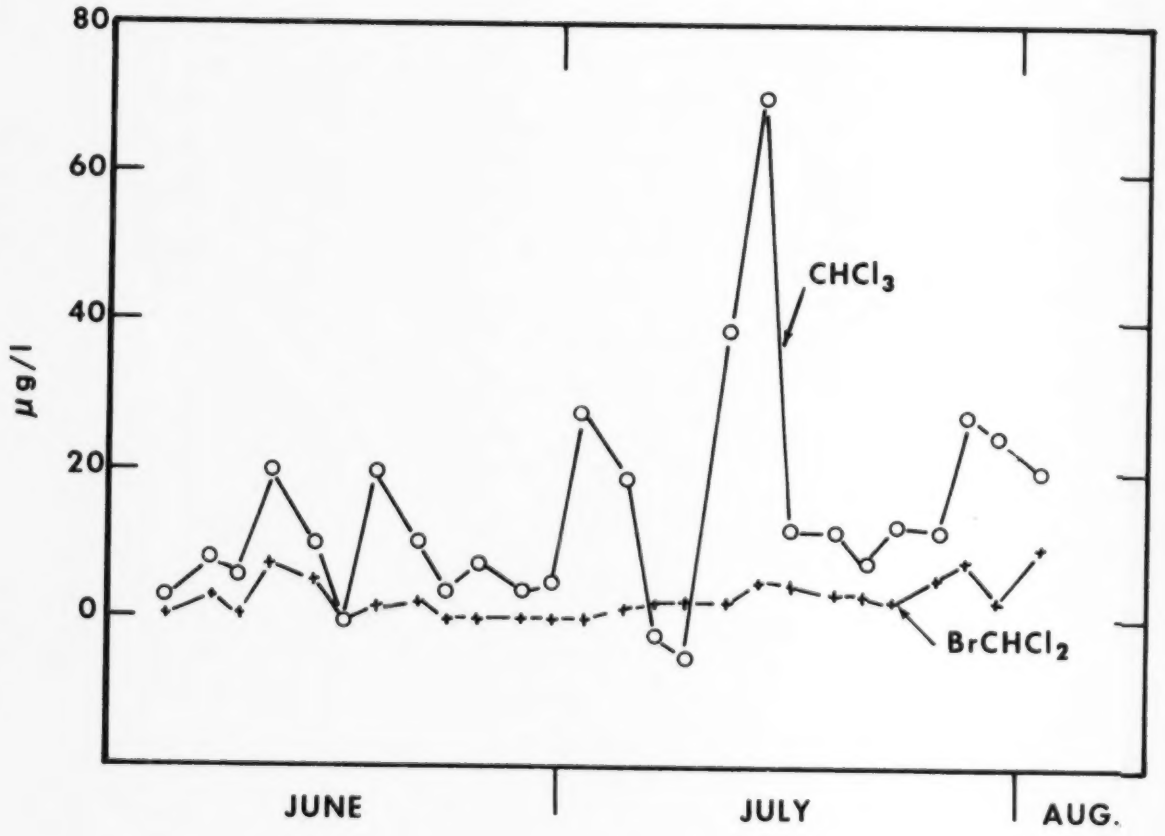


Figure 15. $CHCl_3$ and $BrCHCl_3$ formed during chlorination of first stage carbon effluent.

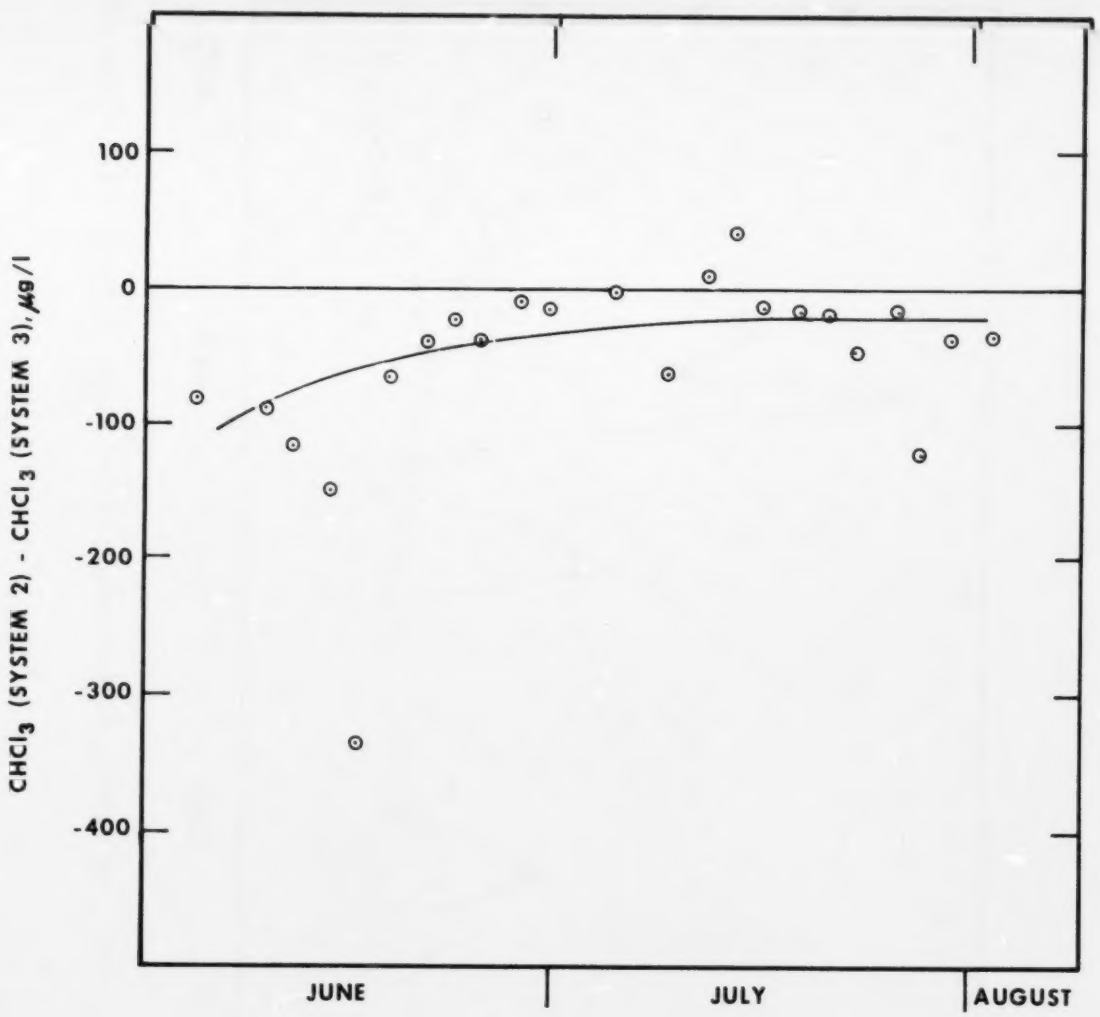


Figure 16. Difference in formation of $CHCl_3$ in system 2 & system 3.

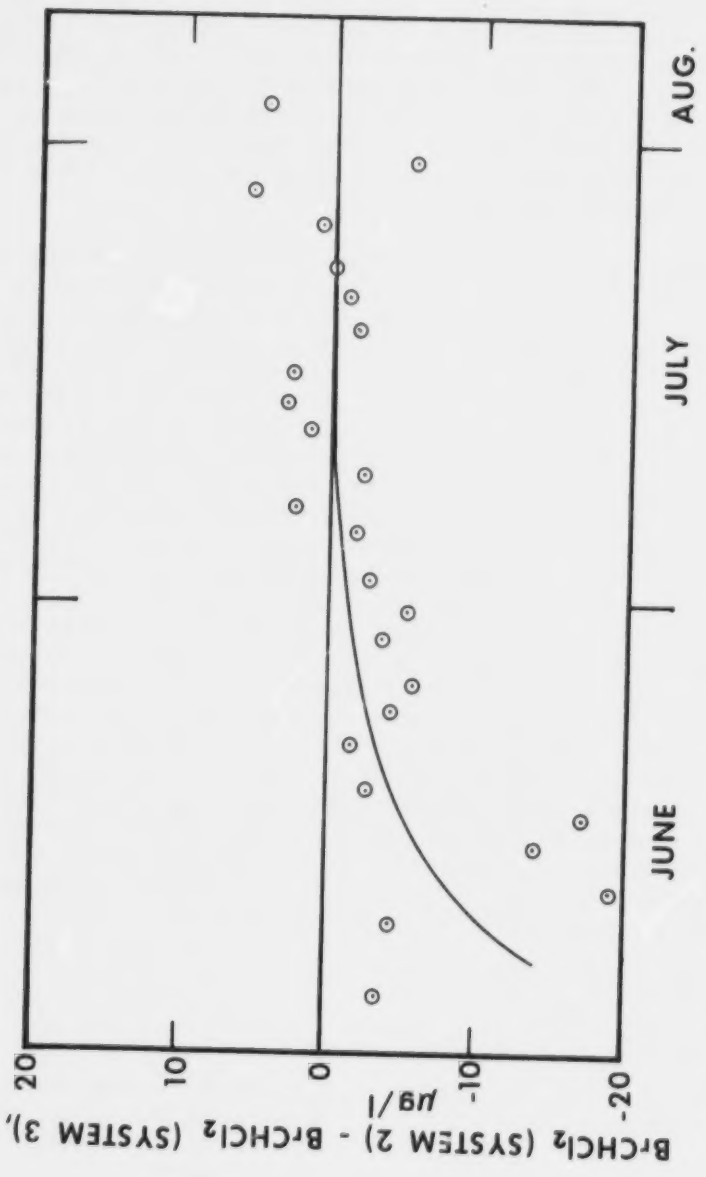


Figure 17. Difference in formation of $BrCHCl_2$ in system 2 and system 3.

commonly employed during disinfection. Table 12 shows the results of long-term chlorine contact with a variety of effluents under a variety of conditions. The effluents listed in the table are as follows: GMF--tertiary lime-filter effluent, the same as designated in the pilot study; GAC--effluent from Carbon System 1 after the carbon had been replaced with fresh carbon; secondary--effluent from the trickling filter system. The results of the breakpoint runs indicate that chlorination of the GMF effluent with a fairly high TOC and high free residual resulted in 600 µg $CHCl_3$/1, while the GAC runs indicate relatively small amounts formed over 40 hours. The use of disinfection dosages resulted in quite low $CHCl_3$ formation ranging from zero to 13 µg/1 formed. It was observed that with disinfection dosages, nearly all the chloroform was produced early in the runs. After 0.5 to 3 hr no additional formation was observed.

A set of short-term (60-min) runs were conducted to observe better the $CHCl_3$ formation with shorter chlorine contact times. The results of these tests are illustrated in Figure 18. These curves are characterized by a very rapid initial rate of formation for the first 2-10 min followed by a general decline in the rate of formation. In one test, chlorination of GAC effluent produced 11 µg $CHCl_3$/1 in the first two minutes and none thereafter. From the results of Figure 18, another factor is added to help explain the lack of correlation of $CHCl_3$ formation in the pilot plant GMF effluent and any other measured parameter. At 4 to 5 min chlorine contact time, the rate of formation is fairly rapid; minor deviations in delivery time of the sample from the reactor to the sample chamber or momentary changes in reactor detention times due to upstream sampling could result in substantial variation in the amount formed before chlorination. A rigorous examination of the factors influencing the formation of trihalomethanes could possibly delineate effects of pH, chlorine residual, wastewater pretreatment, etc. In a real-world wastewater treatment system,however, variations in precursor concentration cannot be measured or predicted instantaneously. Therefore, common sense and the data at hand indicate that if breakpoint chlorination is to be practiced, chlorination of the wastewater at the point of lowest organic concentration with the lowest manageable free residual at neutral pH with the shortest maneageable contact time before dechlorination should result in the minimum production of trihalomethanes. The application of dosages of chlorine which result in only combined residual produce little or no trihalomethane.

GRANULAR ACTIVATED CARBON PERFORMANCE

Removal of Volatile Halogenated Organics

Chloroform was the only compound of the six VHO's that was detected consistently and in significant quantity in the samples taken around the activated carbon and BPC systems. Therefore, the major emphasis in the analysis of carbon performance is on chloroform removal.

As shown in Figure 4, each GAC system is treated as three adsorption systems. For example, GAC System 1 has a 10-min contact time adsorber treating GMF effluent (1A), a 20-min contact time adsorber treating GMF effluent (1A + 1B, designated here 1AB), and a 10-min contact time adsorber

TABLE 12 - BATCH CHLORINATION RESULTS

Effluent	Run Type*	Organic carbon total/soluble mg/l	Cl_2 dose mg/l	Init.Res Cl_2 + free/total mg/l	Final Res. Cl_2 † free/total mg/l	pH	$CHCl_3$ formed § mg/l
GMF	B	20/17	116	36/39	8/9	7.1	600
GAC	B	8.6/8.6	88	25/30	10/20	7.8	30
GAC	B	5.6/4.6	80	8/13	2/6	7.3	27
GMF	D	10/5.8	30	1/20	1/16	8.1	13
Secondary	D	69/16	30	1/16	0/8	7.7	12
Secondary	D	25/13	10	0/7	0/3	7.5	5
GAC	D	1.4/1.2	30	1/20	1/13	7.3	2
GMF	D	8.6/5.8	10	0/3.5	0/2.4	7.7	N#
GAC	D	1.4/1.0	10	0/7	0/4	7.3	N

* B denotes breakpoint chlorination;
D denotes disinfection dosages applied - less than breakpoint.

\+ Initial residual chlorine measured 5 min after hypochlorite addition.
† Final residual chlorine measured 40 hr after hypochlorite addition.
§ Amount formed after 40 hr contact time.
\# None formed.

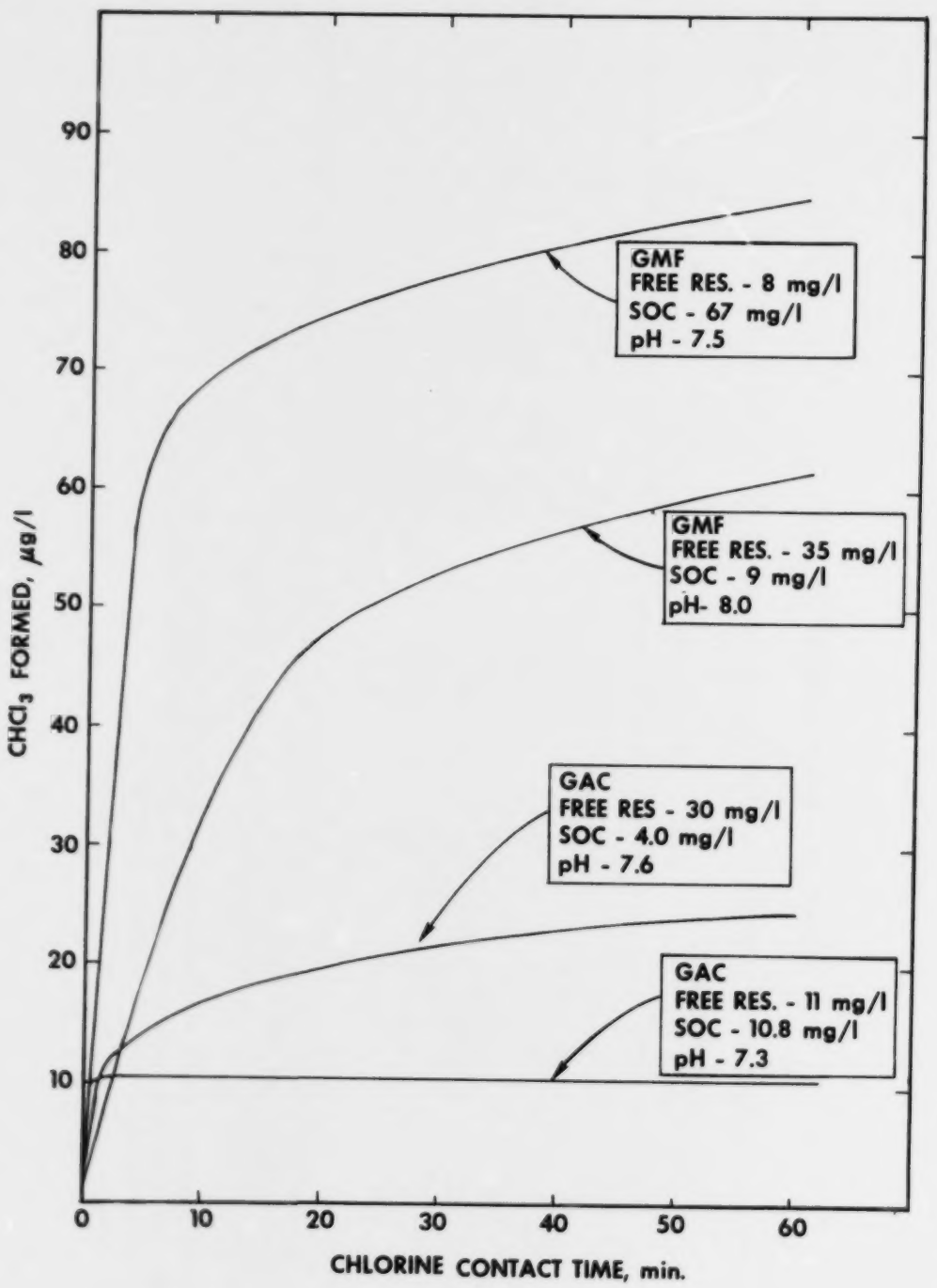


Figure 18. Short-term batch chlorination test results.

treating the effluent from adsorber 1A (1B). The carbon column designations are shown in Table 13. Adsorber 2 AB cannot be considered as a single 20-min system from a VHO removal standpoint because of the breakpoint reactor between stages. As Table 13 indicates, the interpretation of the chloroform removal data for systems 1A, 1AB, 2A and 3AB is hindered because of the extremely large influent chloroform measurement in the samples of July 2. The effect of the large influx of $CHCl_3$ on July 2 on GAC System 1 is shown in Figure 19, in which the $CHCl_3$ concentrations after 10 min and 20 min GAC contact are shown in a time plot. After 10 min contact, the $CHCl_3$ concentration on July 2 was reduced from 2400 µg/1 to 59 µg/1, while none was detected after 20 min contact time. After July 2, the first stage effluent was usually higher than the influent, while the second stage maintained low effluent levels for some time. In fact, the second stage exhibited a fairly uniform breakthrough curve, apparently unaffected by the July 2 event.

The $CHCl_3$ concentrations in the effluents from Columns 3A, 3B, 2B and 1B are shown as a function of volume of wastewater treated in Figures 20, 21, 22, and 23. These effluents were unaffected by the July 2 slug and illustrate the shape of the breakthrough curves and the relatively good fit of the smooth curves to the data points. After the breakthrough of $CHCl_3$ in the effluent of column 3A occurred (Figure 20), the column was kept in service. Its capacity for removal of $CHCl_3$ was essentially exhausted, showing removal only when the influent concentration rose to much higher levels than usual. The effluent from 3A was often higher in $CHCl_3$ than the influent after breakthrough occurred. This phenomenon was also observed in the carbon treatment of chlorinated river water, as described earlier (26).

The four breakthrough curves are shown together in Figure 24 for comparison. Several superficial observations can be made from examination of the breakthrough curves. Locating the breakpoint chlorination system in the mid-carbon position resulted in about 20% longer running time before carbon broke through to a concentration of 5 µg/1. Examination of the breakthrough curves of System 3 for influence of contact time results in a somewhat unexpected observation. Using $CHCl_3$ concentration of 5 or 10 µg/1 as the exhaustion criterion, 20-min contact time allows over 3 times the run length to exhaustion as 10-min contact time.

Love et al. found that doubling the contact time approximately doubled the bed life (26). Other work on the breakthrough of sewage organics showed a 20-min contactor had less than twice the service life of a 10-min contactor with TOC as the effluent criterion (43). Approximately 50 cu m and 165 cu m had been treated in System 3 when the effluents from the first and second stages, respectively, reached a $CHCl_3$ level of 5 µg/1. Since the volume of the 10-min contactor was 0.041 cu m and the volume of the 20-min contactor was 0.082 cu m, the throughputs to an exhaustion criterion of 5 µg $CHCl_3$/1 in the 10-min and 20-min contactors were 1200 and 2000 bed volumes, respectively. Carbon utilization rate can be defined as the weight of carbon exhausted per unit volume of wastewater treated. Using a bed bulk density of 420 kg/cu m, a 20-min contactor would be exhausted at a rate of 200 g carbon/cu m wastewater treated, while the utilization rate of a 10-min contactor would be 340 g/cu m. This is a significant difference in performance which suggests that for a weakly sorbed substance such

TABLE 13 - CARBON COLUMN DESIGNATIONS

Carbon column designation	Contact time (min)	Influent	Remarks
1A	10	GMF	1
1B	10	1A	2
1AB	20	GMF	1
2A	10	GMF	1
2B	10	BK2	2
2AB	-	-	3
3A	10	BK3	4
3B	10	3A	2
3AB	20	BK3	5

Remarks:

1. Influent to 1A, 1AB and 2A included the 2400 µg/l value of July 2. Capacity and breakthrough data are not useful.
2. 1B, 2B, and 3B all received wastewater treated with 10-min carbon contact. The $CHCl_3$ concentrations in their influents are variable but within a reasonable range. Capacity and breakthrough data from these second-stage columns are useful.
3. 2AB cannot be treated as a single 20-min contact time adsorber because of the chlorination reactor which altered the wastewater composition between stages.
4. 3A was exhausted before the July 2, 900 µg/l influent concentration was observed. The capacity and breakthrough data to the point of exhaustion can be used.
5. 3AB was not exhausted at the time the July 2, 900 µg/l influent concentration was observed. Capacity and breakthrough data are only marginally useful.

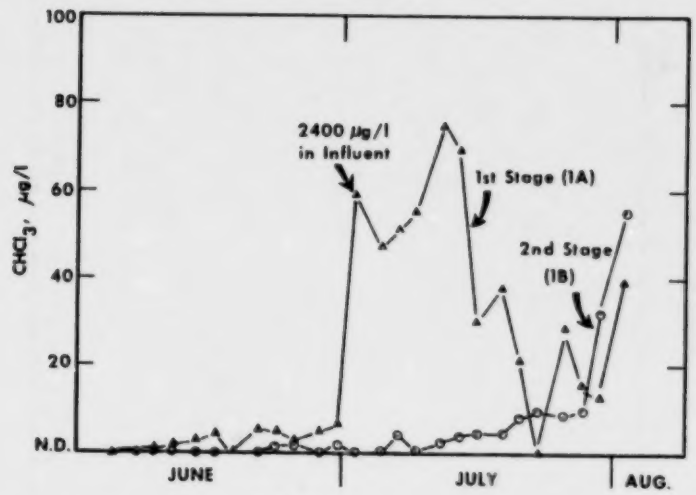


Figure 19. $CHCl_3$ in effluents from GAC system 1.

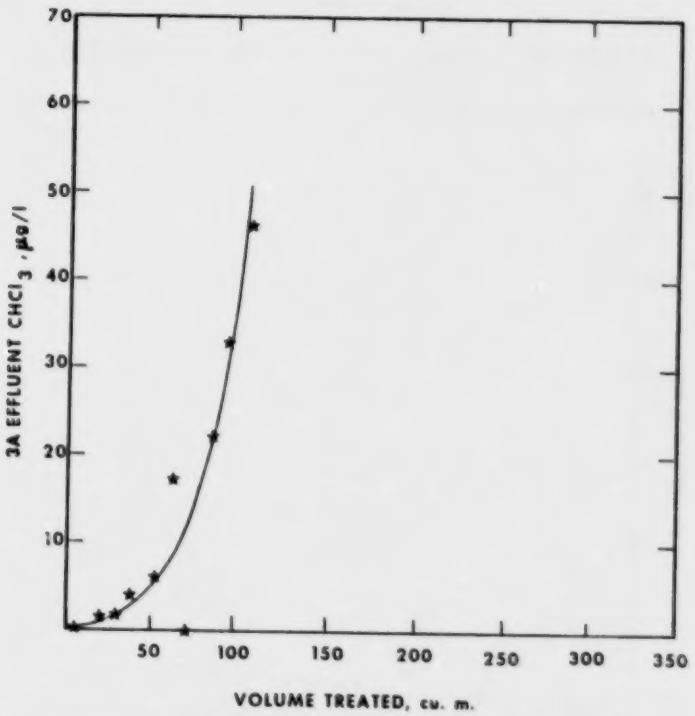


Figure 20. $CHCl_3$ breakthrough, column 3A.

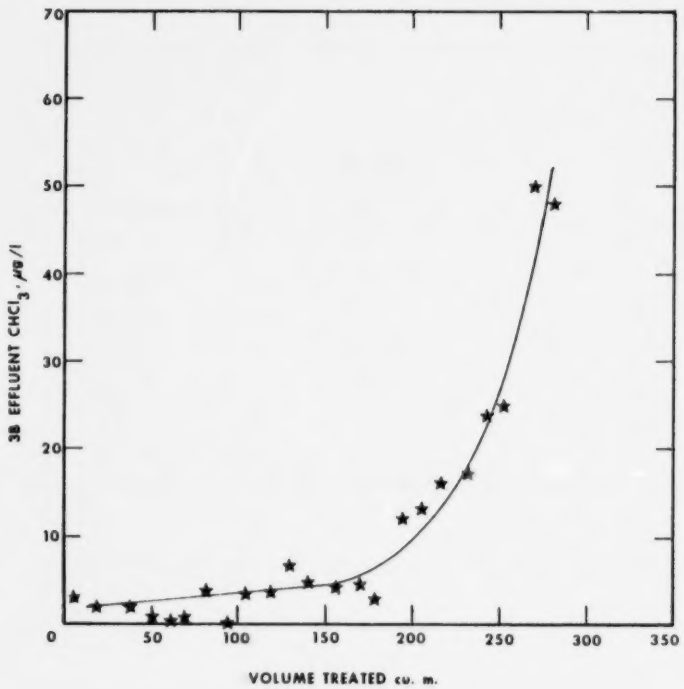


Figure 21. $CHCl_3$ breakthrough, column 3B.

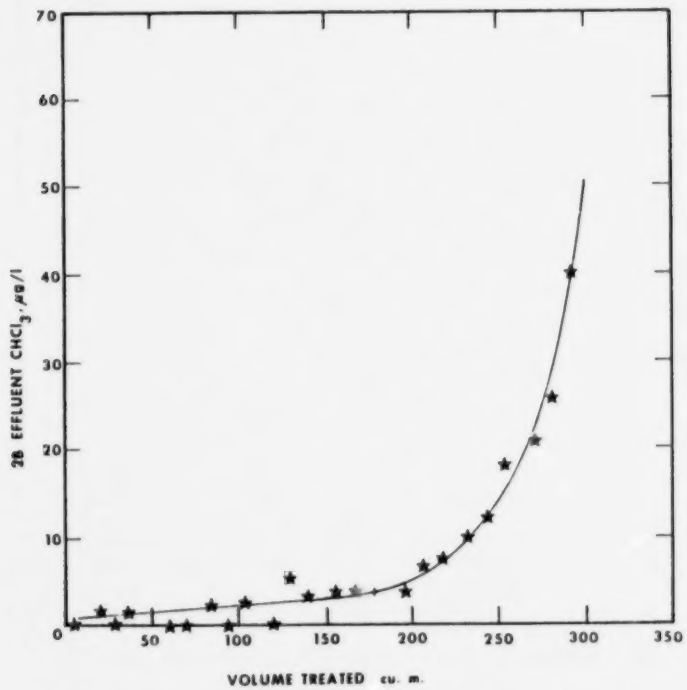


Figure 22. $CHCl_3$ breakthrough, column 2B.

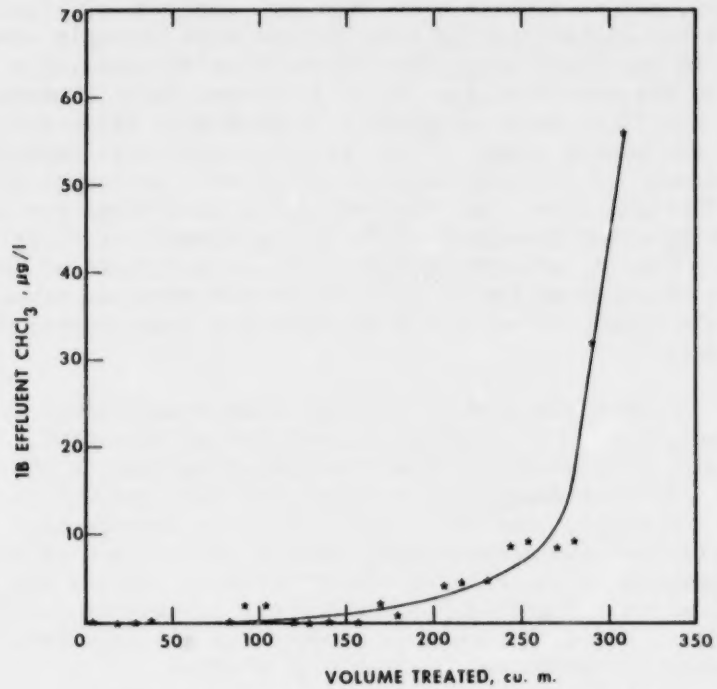


Figure 23. $CHCl_3$ breakthrough, column 1B.

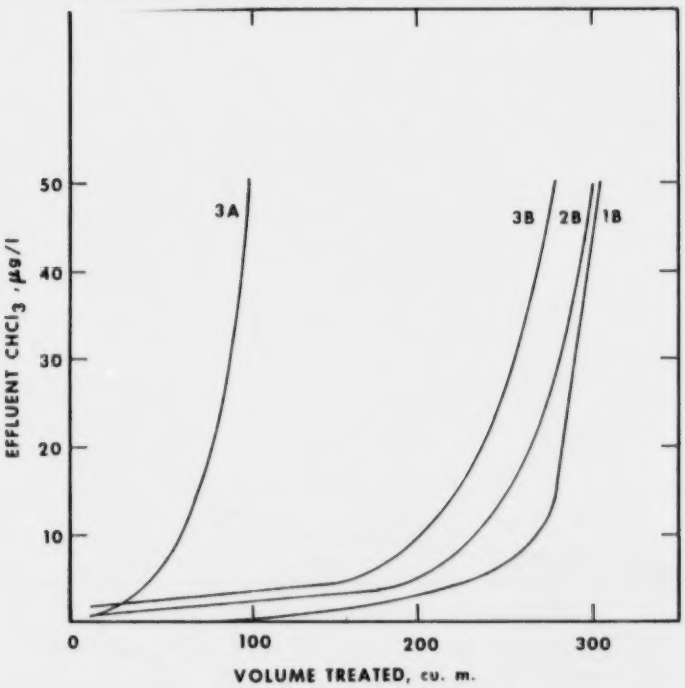


Figure 24. $CHCl_3$ breakthrough curves.

as chloroform, longer contact times may give improved utilization of the carbon. A probable explanation is that because more strongly adsorbed organics are removed in the first stage, the competition for available adsorption sites is reduced in the second stage. As will be seen later, removal of competing organics in the first stage apparently allowed more efficient chloroform adsorption in the second stage. This could be especially important in considerating treatment of polluted surface waters with activated carbon for removal of trihalomethanes. One approach often considered for installation of GAC in drinking water treatment works is replacement of filter sand with GAC. This approach usually results in empty bed contact times of only 4-8 min. A careful examination of the effects of contact time and removal of competing organics could result in lower GAC regeneration requirements for trihalomethane removal.

Figure 25 shows the pattern of chloroform breakthrough as a function of cumulative weight of $CHCl_3$ applied to each 10-min contactor. The cumulative applied loading was calculated from the concentrations in the influent to each carbon column as designated in Table 13, with columns 3A and 3B treated as separate adsorbers. The "B" columns all were second-stage columns treating wastewater that had already been treated with 10-min carbon contact. Column 3A operated on chlorinated filter effluent. While the loading to each column was low, (< 0.3 g $CHCl_3$/kg carbon) all columns produced very low effluent $CHCl_3$. The differences in performance are only apparent as the cumulative loading increases and breakthrough occurs.

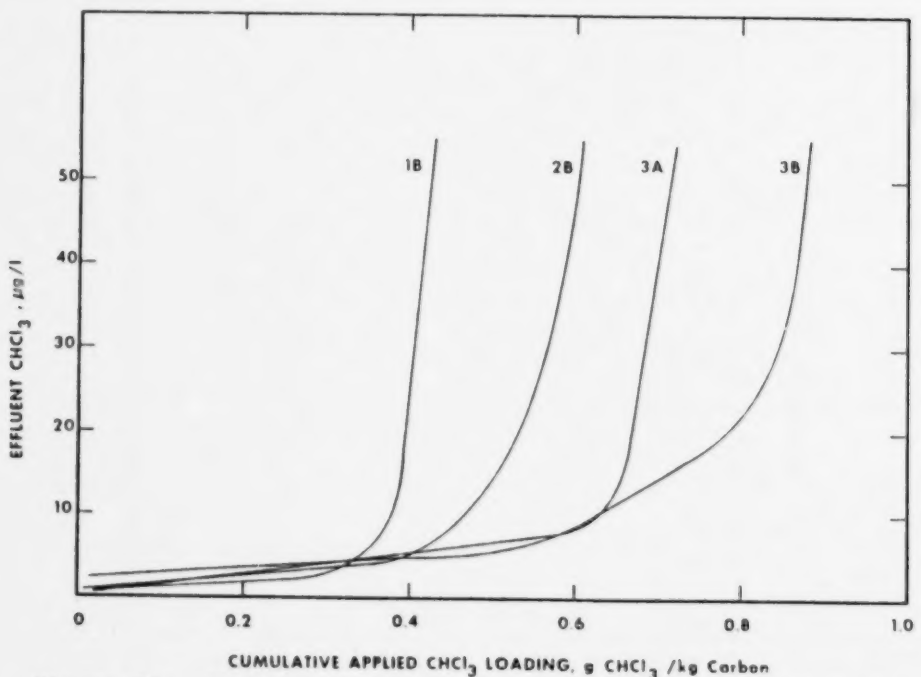


Figure 25. $CHCl_3$ breakthrough as a function of applied $CHCl_3$.

Table 14 shows the capacity of the carbon for chloroform removal in each of the 10-min columns. Carbon capacity is defined as the cumulative weight of $CHCl_3$ removed per unit weight of carbon up to some point in the service time of the carbon. Values shown are for effluent breakthrough concentrations of 5 µg/l and 10 µg/l and also for the maximum capacity observed before complete exhaustion. As is evident from Figure 25, nearly all the applied chloroform was removed up to the time of breakthrough. Therefore, the values in Table 14 reflect the same pattern as Figure 25. Very little difference in carbon capacity can be detected at a 5 µg/l effluent level. At the 10 µg/l effluent level, 1B had removed less $CHCl_3$ than 2B, while 3A and 3B had both removed substantially greater amounts of $CHCl_3$ than 2B. At the point of zero removal or complete exhaustion, column 3B had exhibited greater capacity for chloroform removal than 3A.

TABLE 14 - CAPACITY OF CARBON FOR $CHCl_3$ REMOVAL*

Item	g $CHCl_3$ removed/g carbon			
	3A	3B	2B	1B
At 5 g $CHCl_3$ breakthrough	0.36	0.38	0.37	0.32
At 10 g/1 $CHCl_3$/ breakthrough	0.61	0.62	0.43	0.35
Maximum capacity	0.64	0.74	0.47	0.35

*Ten minute contact time.

The maximum capacity values are further illustrated in Figure 26 where they are plotted against the flow weighted average concentration of $CHCl_3$ in the influents to each 10-min contractor up to the time of zero removal in an equilibrium type plot. The average influent concentration is analogous to the equilibrium concentration of solute, and the maximum capacity can be considered the capacity at equilibrium. The three second-stage columns fit a Freundlich type equation very well:

$$\frac{X}{M}_{max} = 0.022 \; C_{inf}^{0.87} \qquad [5]$$

where $\frac{X}{M}$ max = maximum capacity at complete exhaustion, $\frac{\text{g } CHCl_3 \text{ removed}}{\text{kg carbon}}$

and C_{inf} = flow weighted average influent concentration, µg $CHCl_3$/1.

The data point for column 3A lies below this line of best fit for the B columns indicating less efficient adsorption by 3A. The B columns all treated wastewater which had been treated with 10 min contact with GAC, while 3A treated GMF effluent. It appears from Figure 26 that the $CHCl_3$ adsorption characteristics of the three B columns were similar even though the loading pattern was variable throughout the study and among the three columns. Another point of interest is that column 2B influent contained an average of 12 mg/1 total chlorine residual of which 8.4 mg/1 was free chlorine residual.

Figure 26 indicates no effect of chlorine on the $CHCl_3$ removal capacity of column 2B.

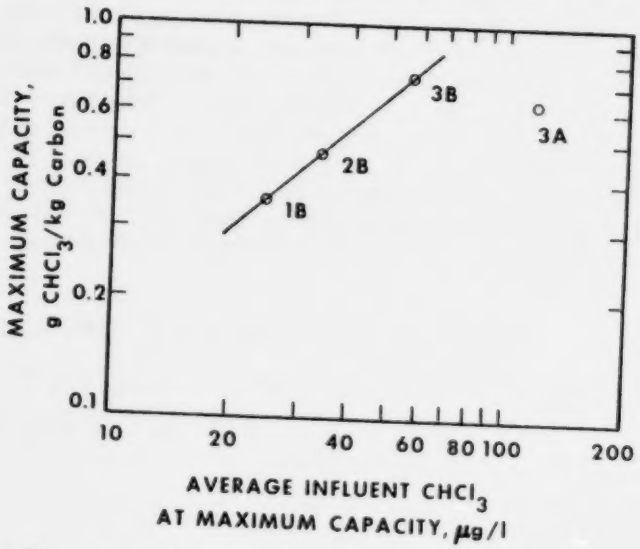


Figure 26. Capacity of 10-min contactors for $CHCl_3$ removal.

The less efficient removal of $CHCl_3$ by column 3A is almost certainly caused by competition of more strongly adsorbed sewage organics for adsorption sites. Removal of these sewage organics by the A columns reduces the competition for sites in the B columns and permits more efficient removal of chloroform in the second stage columns.

A laboratory batch equilibrium adsorption test was run using $CHCl_3$ in carbon-treated distilled water to which minerals had been added to simulate the salt content of sewage. (43) In this test the resulting equilibrium expression resulted:

$$\frac{X}{M} = 0.033\ C_{eq}^{0.84} \qquad [6]$$

where $\frac{X}{M}$ = weight of $CHCl_3$ removed per unit weight of carbon, g $CHCl_3$/kg carbon

C_{eq} = concentration of $CHCl_3$ in the liquid phase at equilibrium, µg $CHCl_3$/l.

This isotherm line, if plotted on Figure 26, would lie above the B column data with nearly the same slope. This could imply that the organics discharged from the A columns did reduce the efficiency of the B columns for chloroform removal when compared with a $CHCl_3$ solution free of sewage organics.

While a great deal should not be made of the comparison of the B column data with the results of one batch test, it is encouraging that the capacity-concentration relationship obtained from the column data taken over a period of 9 1/2 weeks under highly variable conditions appears reasonable in the light of the laboratory results. The system was not designed to obtain data for comparisons between batch and column tests. If that were the objective, numerous isotherms run on the wastewater actually being fed to the columns and columns spiked with known, constant concentrations of $CHCl_3$ would have been more useful.

The column data indicate that in a wastewater of a given quality, the capacity of carbon for removal of chloroform can be directly related to the influent concentration by a Freundlich-type expression. It is also apparent that the presence of competing organics can greatly reduce the efficiency of chloroform removal. For example, if column 3A had functioned as efficiently as the three B columns for $CHCl_3$ removal (if it had conformed to Eq [5] at its average influent concentration of 119 µg/l), its capacity would have been 1.41 g/kg, more than double its actual capacity. The data also indicate that applying an average of 12 mg/l total residual chlorine does not diminish the efficiency of carbon for removing chloroform.

Data on the removal of $BrCHCl_2$, Br_2CHCl, CCl_4 and $C_2H_4Cl_2$ are shown in the Appendix. Bromoform was never detected in the effluent of any of the carbon columns. $BrCHCl_2$ was nearly always found in the influent to carbon system 3. The first detectable $BrCHCl_2$ in the effluent from 3A occurred after 2000 bed volumes of chlorinated filter effluent with an average concentration of 12 µg/l had been treated. At that time 0.06 g $BrCHCl_2$/kg carbon had been removed. If column 3AB is considered as a whole, consistent breakthrough was not observed until 3500 bed volumes had been treated. These data show the same effect of more efficient removal by the second stage than the first stage as was evident from the chloroform data.

Carbon tetrachloride began appearing consistently in the effluents from all three A columns when ~ 2500 bed volumes had been treated. The B columns contained CCl_4 only in two to three samples throughout the project and then in very low concentrations (< 2 µg/l). The amounts of the other specific organics in the carbon influents were too low and were present too infrequently to merit discussion.

Removal of Extractable Organic Chlorine

Table 15 gives the concentrations of extractable organic chlorine in the composite samples taken on the three dates shown. With low influent levels the carbon effluents in Systems 1 and 2 contained less than 2 µg/l in all samples. However, with an increase with time on stream System 3 showed some evidence of breakthrough of organic chlorine in the effluent of each stage. On the third sample set (the last day of the project) the first stage carbon (3A) removed only 5% of its influent organic chlorine, while the final effluent showed 80% removal. The data are very limited and supply only order of magnitude indications of removal of extractable organic chlorine by activated carbon. The more heavily loaded carbon system showed signs of

organic chlorine breakthrough, although this was not as rapid as chloroform breakthrough.

TABLE 15 - EXTRACTABLE ORGANIC CHLORINE*

Date	F	1A+	1B	2A	BK2	2B	BK3	3A	3B
6/25	3.7	N+	N	N	2.0	N	6.5	0.2	N
7/9	6.6	1.6	1.1	1.8	3.1	1.7	11.5	3.8	1.5
8/9	2.3	N	N	1.3	6.7	N	27.7	26.5	5.2

*All values - µg organic chlorine/1.

+Sample designations refer to Figure 4.

†N- Not detected.

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APPENDIX

VOLATILE HALOGENATED ORGANICS DATA

TABLE A-1 - $CHCl_3$*

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	26	N	N	N	2.5	N	110	N	2.6
7	19	20	0.5	N	N	7.7	1.7	86	1.5	1.8
9	29	14	0.9	N	N	5.7	N	104	1.6	N
11	37	12	1.5	0.4	N	20	1.3	150	4.1	1.9
14	50	9.5	2.3	N	2.1	12	N	170	6.0	0.8
16	61	5.5	4.1	N	4.0	3.3	N	340	17	0.4
18	69	10	N	N	3.1	23	N	96	N	0.9
21	83	5.4	5.2	N	9.4	19	2.3	53	22	3.6
23	93	9.3	4.4	1.9	9.3	13	N	39	33	N
25	104	4.8	2.5	1.8	6.0	13	2.7	48	46	3.3
28	119	3.3	4.9	N	9.5	13	N	20	74	3.5
30	129	11	6.1	2.0	8.5	13	5.4	44	83	6.7
7/2	140	2400	59	N	47	75	3.4	900	104	4.4
5	157	15	47	N	43	62	3.6	35	67	4.2
7	168	150	51	2.0	41	39	3.6	45	119	4.5
9	178	19	55	0.7	63	58	3.6	75	77	2.9
12	195	24	75	2.5	47	86	3.7	52	133	12
14	206	33	69	3.9	4.8	76	6.7	63	131	13
16	217	11	25	4.7	28	40	7.3	37	67	16
19	232	N	38	4.5	38	50	10	29	76	17
21	243	N	21	8.7	23	31	12	27	51	24
23	253	N	N	9.3	23	36	18	59	53	25
26	270	N	28	8.3	17	29	21	28	29	50
28	281	2.8	15	9.4	11	39	26	152	21	48
30	292	4.9	12	32	15	41	40	62	39	80
8/2	308	13	40	55	37	57	94	67	70	150
6	+325									
9	+342									

* All values µg/l.

\+ Problems in Analysis - $CHCl_3$ data for 8/6 and 8/9 not available.

N - denotes not detected. For sample designations refer to Figure 4.

TABLE A-2 - $BrCHCl_2$ *

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	2.7	N+	N	N	N	N	6.0	N	N
7	19	2.8	N	N	N	2.8	N	7.0	N	N
9	29	2.8	N	N	N	0.3	N	7.3	N	N
11	37	1.5	N	N	N	7.4	N	23	N	N
14	50	N	N	N	N	5.1	N	19	N	N
16	61	1.9	N	N	N	N	N	19	N	N
18	69	1.6	N	N	2.0	3.8	N	6.0	N	N
21	83	1.9	N	N	N	2.5	N	6.3	1.8	N
23	93	N	N	N	N	N	N	4.4	3.0	N
25	104	N	N	N	N	N	N	5.5	2.5	N
28	119	N	N	N	N	N	N	3.5	4.1	N
30	129	N	N	N	N	N	N	5.2	N	N
7/2	140	N	N	N	N	N	N	2.7	4.0	N
5	157	N	N	N	N	1.8	N	3.5	3.3	N
7	168	N	N	N	N	2.2	N	N	4.3	N
9	178	N	N	N	N	2.5	N	4.5	2.4	N
12	195	2.7	N	N	N	2.1	N	3.5	5.5	N
14	206	3.6	N	N	N	5.2	N	5.7	8.1	N
16	217	4.6	N	N	N	4.8	N	6.9	6.7	N
19	232	N	N	N	N	3.3	N	5.1	8.5	N
21	243	N	N	N	N	3.7	N	4.8	5.7	2.6
23	253	N	N	N	N	2.9	N	2.9	2.7	N
26	270	N	N	N	N	5.5	N	4.7	4.8	N
28	281	N	N	N	N	8.2	N	3.9	5.9	N
30	292	1.0	N	N	N	7.5	2.5	8.7	8.9	4.9
8/2	308	3.5	1.3	0.2	0.9	11	4.2	9.0	27	6.0
6	325	3.9	N	N	1.4	26	5.5	8.4	13	8.7
9	342	2.2	0.4	0.6	0.6	2.8	5.6	4.2	8.8	7.5

* All values µg/1. For sample designations refer to Figure 4.
\+ N - denotes not detected.

TABLE A3 - Br_2CHCl*

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	3.4	N+	N	N	N	N	4.8	N	N
7	19	6.0	N	N	N	2.1	N	5.3	N	N
9	29	8.5	N	N	N	1.0	N	9.5	N	N
11	37	1.9	N	N	N	4.7	N	12	N	N
14	50	N	8	N	N	4.1	N	10	N	N
16	61	3.0	N	N	N	N	N	9.8	N	N
18	69	1.4	N	N	N	1.0	N	5.0	N	N
21	83	N	N	N	N	N	N	5.8	N	N
23	93	N	N	N	N	N	N	N	N	N
25	104	N	N	N	N	N	N	N	N	N
28	119	N	N	N	N	N	N	3.2	N	N
30	129	N	N	N	N	N	N	4.7	N	N
7/2	140	N	N	N	N	N	N	N	N	N
5	157	N	N	N	N	N	N	5.7	N	N
7	168	3.6	N	N	N	N	N	N	N	N
9	178	N	N	N	N	N	N	2.8	2.7	N
12	195	N	N	N	N	N	N	2.0	1.1	N
14	206	2.6	N	N	N	N	N	N	2.5	N
16	217	8.9	N	N	N	N	N	6.1	N	N
19	232	9.7	N	N	N	N	N	17	N	N
21	243	N	N	N	N	N	N	N	N	N
23	253	N	N	N	N	N	N	N	N	N
26	270	N	N	N	N	N	N	N	N	N
28	281	N	N	N	N	N	N	N	N	N
30	292	4.1	N	N	N	N	N	N	N	N
8/2	308	1.6	.4	N	N	5.9	0.2	4.0	5.0	0.4
6	325	1.7	N	N	.4	6.3	0.8	3.1	6.2	1.2
9	342	1.1	N	N	N	0.8	0.8	1.0	3.9	0.8

* All values µg/l. For sample designations refer to Figure 4.
\+ N - denotes not detected.

TABLE A-4 - $CHBr_3$ *

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	N+	N	N	N	N	N	17	N	N
7	19	N	N	N	N	N	N	N	N	N
9	29	N	N	N	N	N	N	N	N	N
11	37	N	N	N	N	N	N	22	N	N
14	50	N	N	N	N	N	N	20	N	N
16	61	N	N	N	N	N	N	N	N	N
18	69	N	N	N	N	N	N	N	N	N
21	83	N	N	N	N	N	N	N	N	N
23	93	N	N	N	N	N	N	N	N	N
25	104	N	N	N	N	N	N	N	N	N
28	119	N	N	N	N	N	N	N	N	N
30	129	N	N	N	N	N	N	N	N	N
7/2	140	N	N	N	N	N	N	N	N	N
5	157	N	N	N	N	N	N	N	N	N
7	168	N	N	N	N	N	N	N	N	N
9	178	N	N	N	N	N	N	N	N	N
12	195	N	N	N	N	N	N	N	N	N
14	206	N	N	N	N	N	N	N	N	N
16	217	N	N	N	N	N	N	N	N	N
19	232	N	N	N	N	N	N	N	N	N
21	243	N	N	N	N	N	N	N	N	N
23	253	N	N	N	N	N	N	N	N	N
26	270	N	N	N	N	N	N	N	N	N
28	281	N	N	N	N	N	N	N	N	N
30	292	N	N	N	N	N	N	N	N	N
8/2	308	N	N	N	N	N	N	0.4	N	N
6	325	N	N	N	N	0.8	N	N	N	N
9	342	N	N	N	N	N	N	N	N	N

* All values µg/l. For sample designations refer to Figure 4.
\+ N - denotes not detected.

TABLE A-5 - CCl_4 *

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	1.1	N+	N	N	N	N	2.3	N	N
7	19	N	0.5	N	N	0.6	N	3.5	N	N
9	29	43	0.9	N	N	0.2	N	58	N	N
11	37	N	N	N	N	N	N	N	N	N
14	50	N	N	N	N	N	N	N	N	N
16	61	N	N	N	N	N	N	N	N	N
18	69	N	N	N	N	N	N	N	1.3	1.0
21	83	N	N	N	N	N	N	N	N	N
23	93	N	N	N	N	N	N	N	2.5	N
25	104	3.2	1.9	N	1.5	1.8	N	4.5	3.2	N
28	119	1.0	N	N	9.8	2.8	N	2.3	4.6	N
30	129	9.4	2.5	N	2.6	2.0	N	11	4.1	N
7/2	140	N	4.0	N	N	2.5	N	N	N	N
5	157	2.2	3.6	N	3.6	2.4	N	1.0	4.0	N
7	168	N	2.8	N	2.7	2.3	N	N	3.8	N
9	178	2.0	2.3	N	1.4	2.1	N	2.5	2.0	N
12	195	2.5	3.8	N	N	N	N	3.0	7.0	N
14	206	4.1	4.4	N	N	5.8	N	3.3	7.2	N
16	217	6.5	3.7	N	0.9	3.6	N	4.0	8.6	N
19	232	N	4.7	N	3.7	4.8	N	N	6.6	N
21	243	N	2.5	N	3.3	1.8	N	4.4	4.1	N
23	253	N	2.9	1.0	3.9	2.0	1.0	14	2.5	N
26	270	N	4.0	N	4.0	3.0	1.7	3.1	4.7	N
28	281	1.1	3.0	N	2.8	4.0	N	7.8	2.0	N
30	292	N	2.5	N	2.1	3.6	N	2.0	6.2	N
8/2	308	N	3.1	0.4	2.7	3.3	0.9	0.8	1.0	0.9
6	325	N	N	N	N	0.6	N	3.4	3.0	N
9	342	N	N	N	N	N	N	N	N	N

* All values µg/l. For sample designations refer to Figure 4.
\+ N - denotes not detected.

TABLE A-6 - $C_2H_4Cl_2$ *

Date	Cu m treated	F	1A	1B	2A	BK2	2B	BK3	3A	3B
6/4	5	5.4	N+	N	N	N	N	5.2	N	N
7	19	3.2	N	N	N	N	N	N	N	N
9	29	1.1	N	N	N	N	N	N	N	N
11	37	44	N	N	N	N	N	59	0.8	N
14	50	8.6	1.6	N	N	N	N	9.6	1.9	N
16	61	6.4	1.1	N	N	2.9	N	8.0	1.0	N
18	69	7.9	N	N	N	2.9	N	6.7	N	N
21	83	26	1.3	N	2.6	2.6	N	21	2.7	N
23	93	20	1.4	N	1.6	N	N	7.0	N	N
25	104	N	9.5	N	N	N	N	N	N	N
28	119	N	N	N	N	N	N	N	N	N
30	129	N	N	N	N	N	N	N	N	N
7/2	140	N	N	N	N	5.7	N	7.2	7.1	N
5	157	N	N	N	N	N	N	N	N	N
7	168	N	N	N	N	N	N	N	N	N
9	178	N	N	N	N	N	N	N	N	N
12	195	N	N	N	N	N	N	N	N	N
14	206	N	N	N	N	N	N	N	N	N
16	217	N	N	N	N	N	N	N	N	N
19	232	N	N	N	N	N	N	N	N	N
21	243	N	N	N	N	N	N	N	N	N
23	253	N	N	N	N	N	N	N	N	N
26	270	N	N	N	N	N	N	N	N	N
28	281	N	N	N	N	N	N	N	N	N
30	292	N	N	N	N	N	N	N	N	N
8/2	308	N	N	N	N	N	N	N	N	N
6	325	N	N	N	N	N	N	N	N	N
9	342	N	N	N	N	N	N	N	N	N

* All values µg/l. For sample designations refer to Figure 4.
\+ N - denotes not detected.

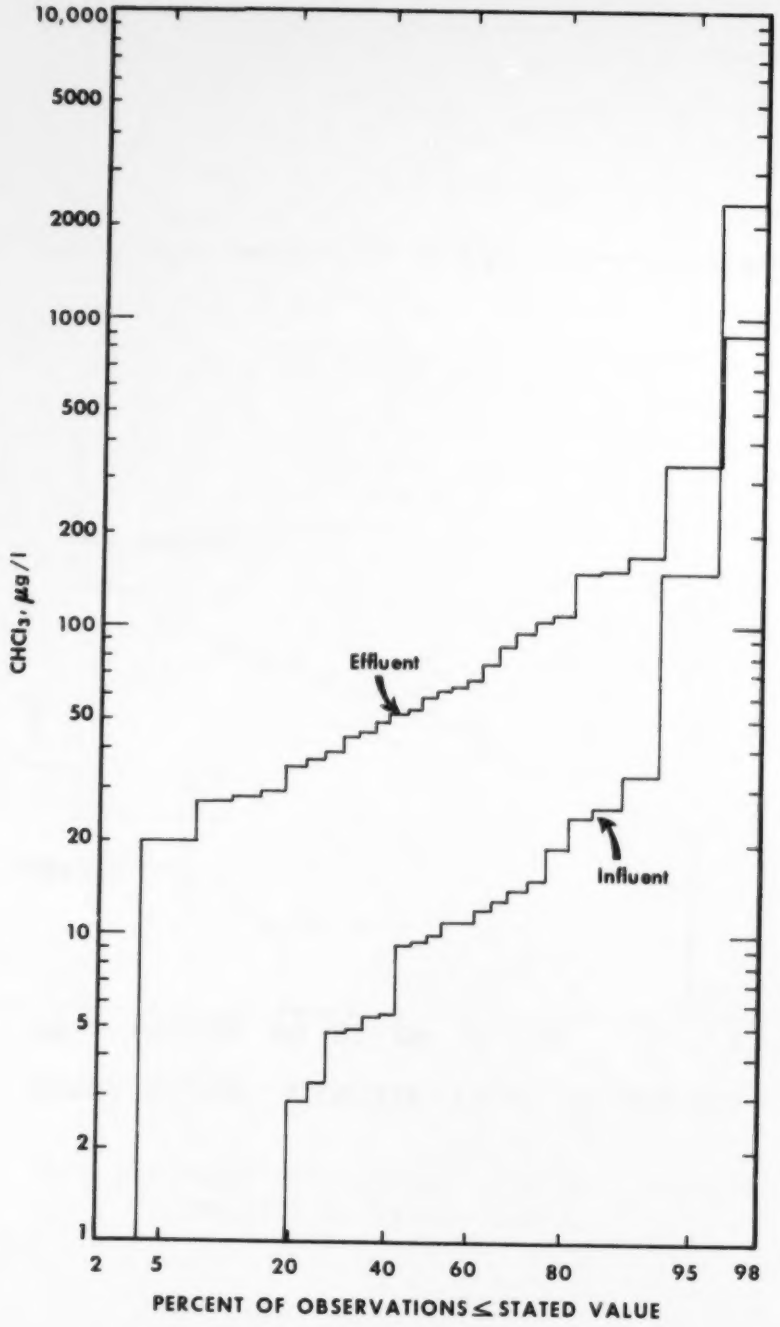

Figure A1. $CHCl_3$ concentrations before and after chlorination of GIF effluent.

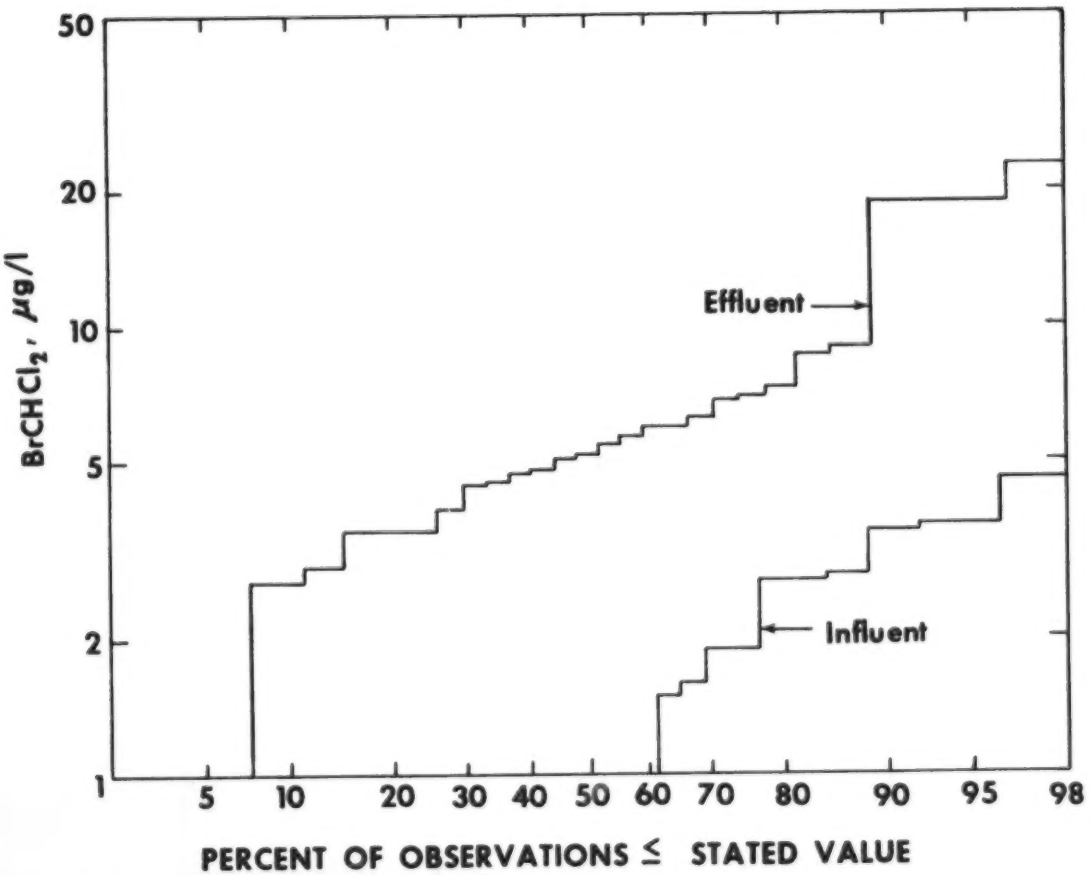

Figure A2. $BrCHCl_2$ concentrations before and after chlorination of GMF effluent.

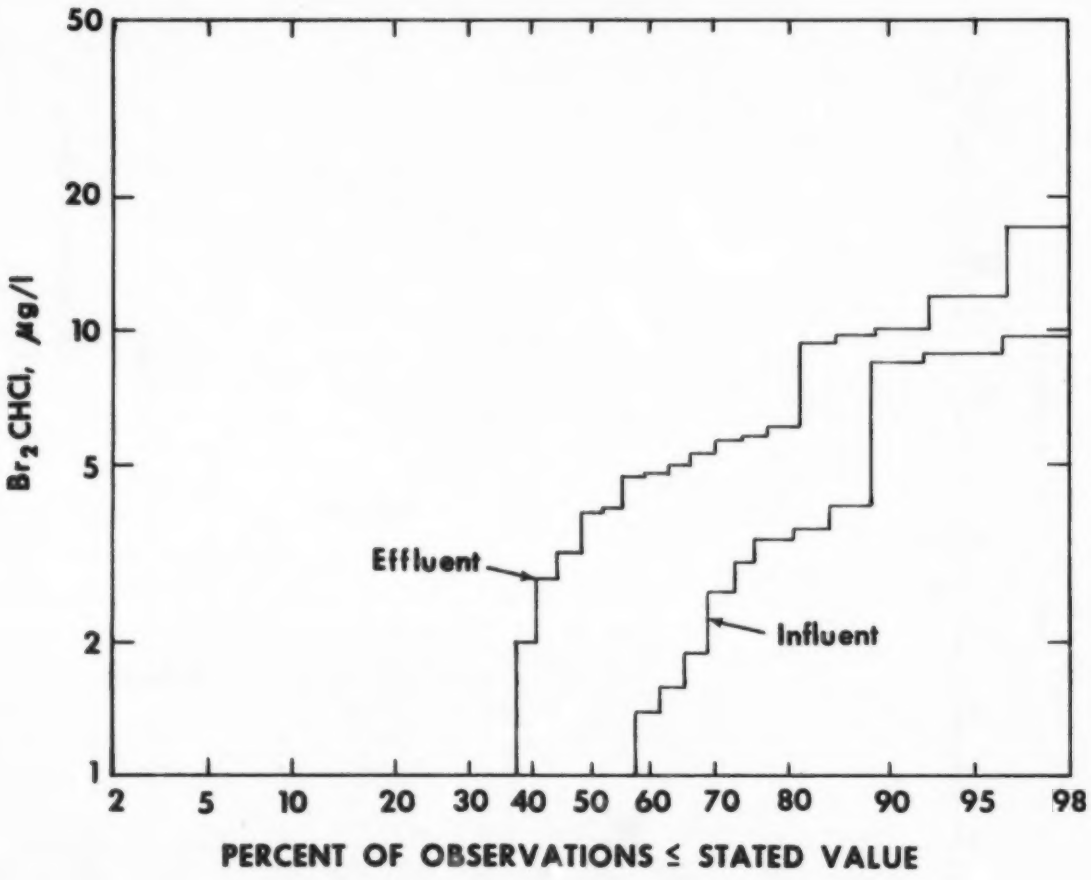

Figure A3. Br_2CHCl concentrations before and after chlorination of GMF effluent.

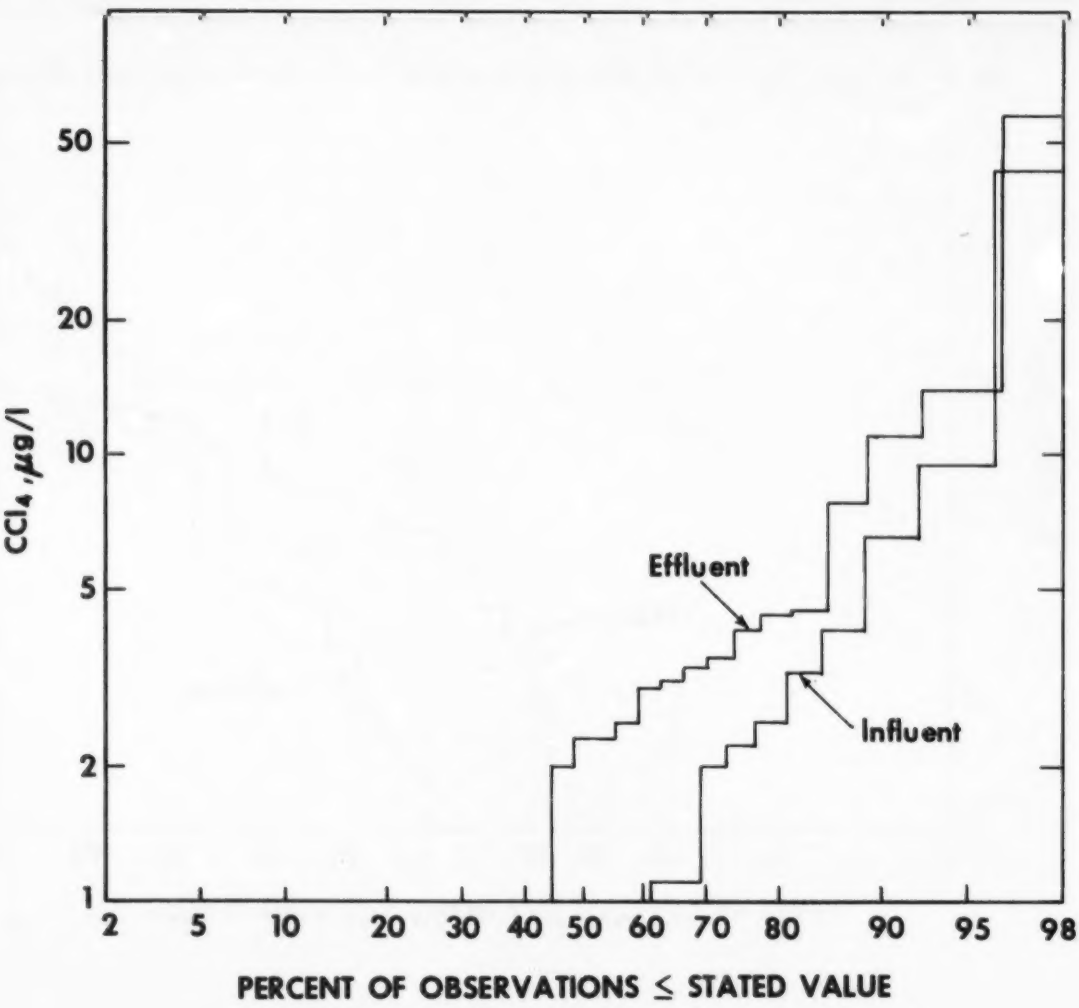

Figure A4. CCl_4 concentrations before and after chlorination of GAF effluent.

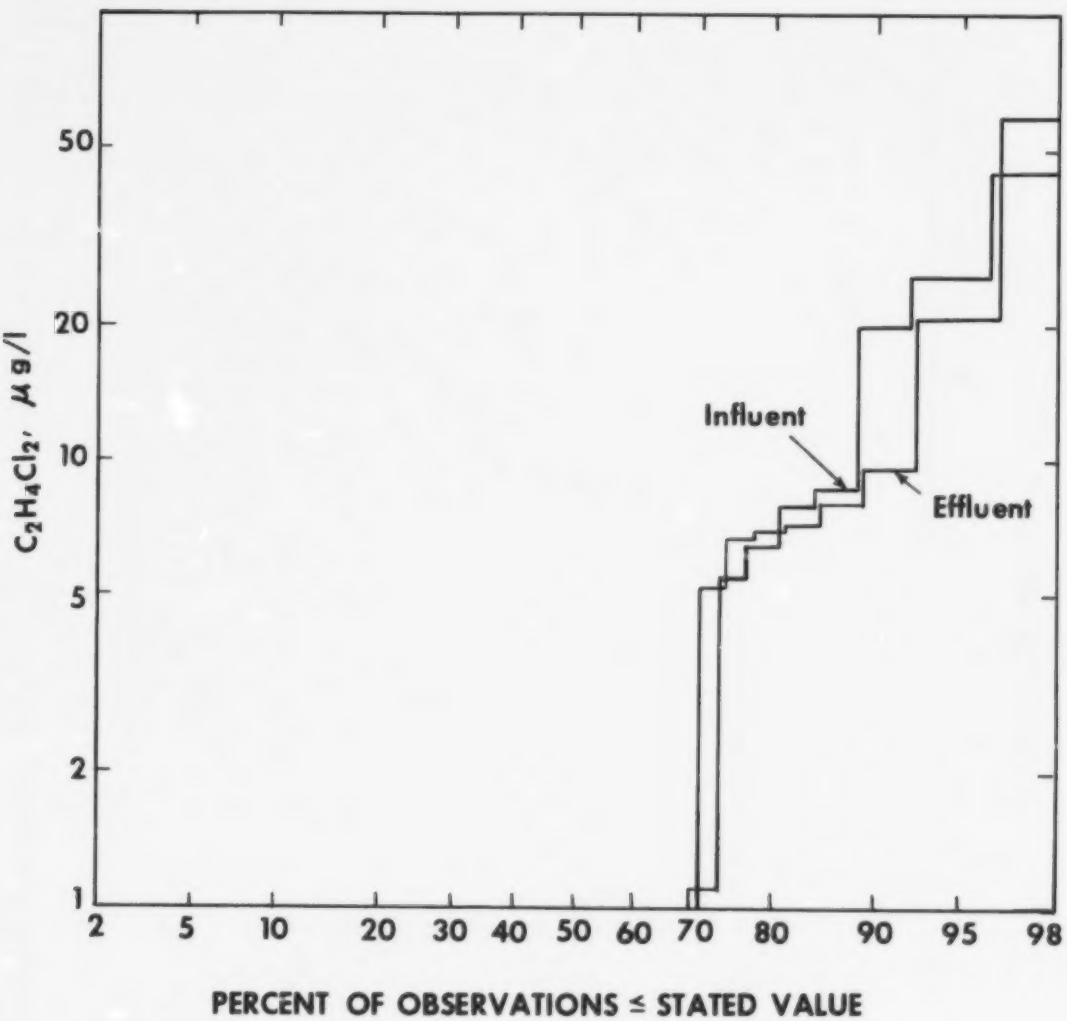

Figure A5. $C_2H_4Cl_2$ concentrations before and after chlorination of GMF effluent.

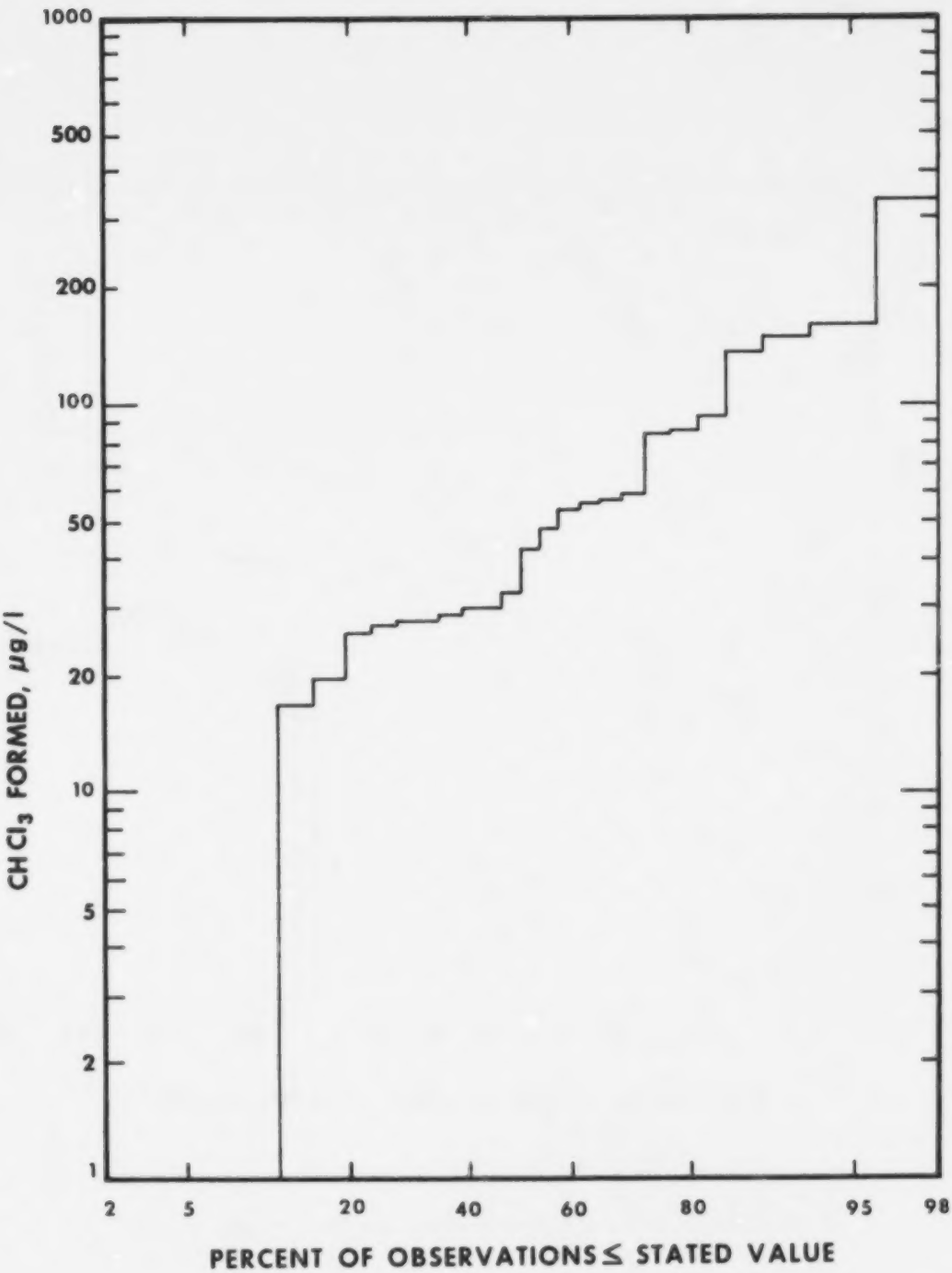

Figure A6. $CHCl_3$ formed during chlorination of GMF effluent.

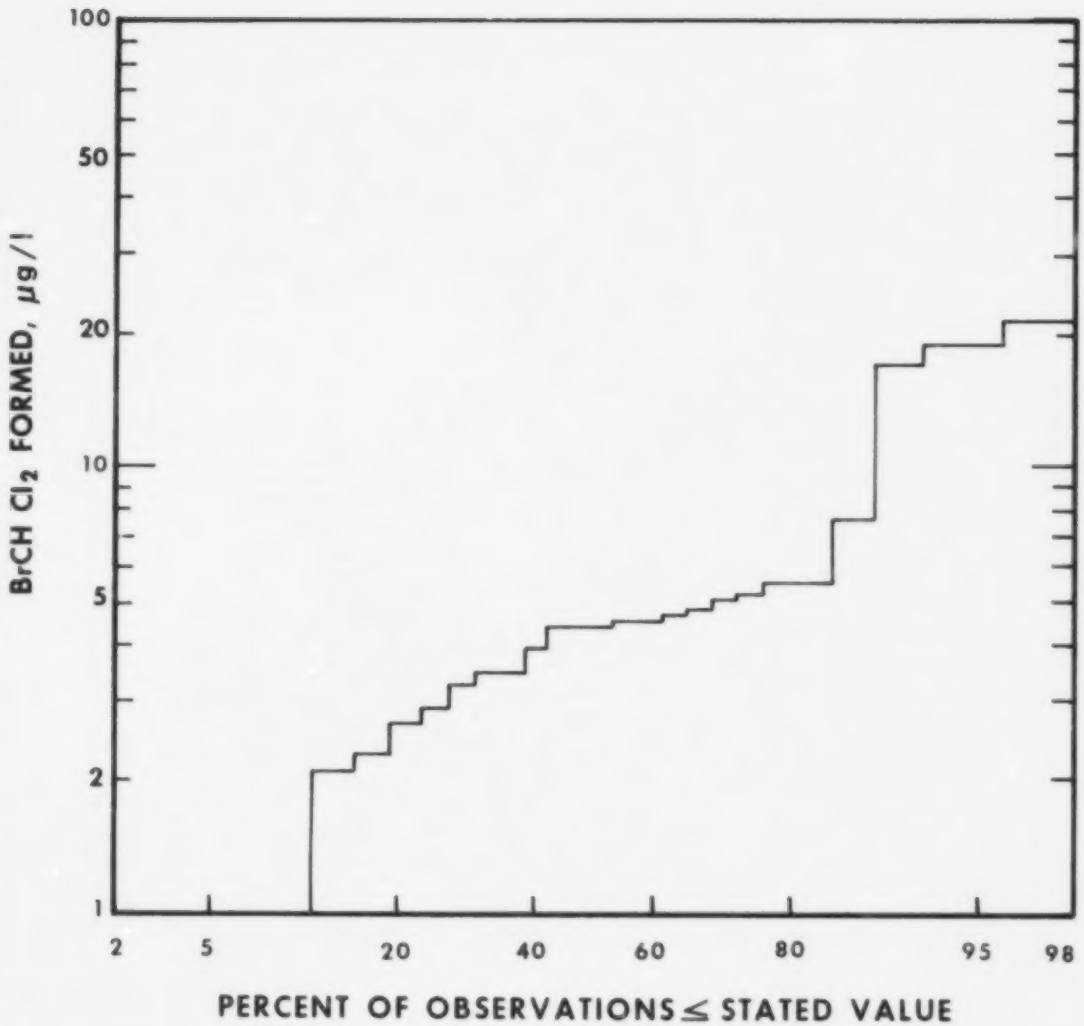

Figure A7. $BrCHCl_2$ formed during chlorination of GMF effluent.

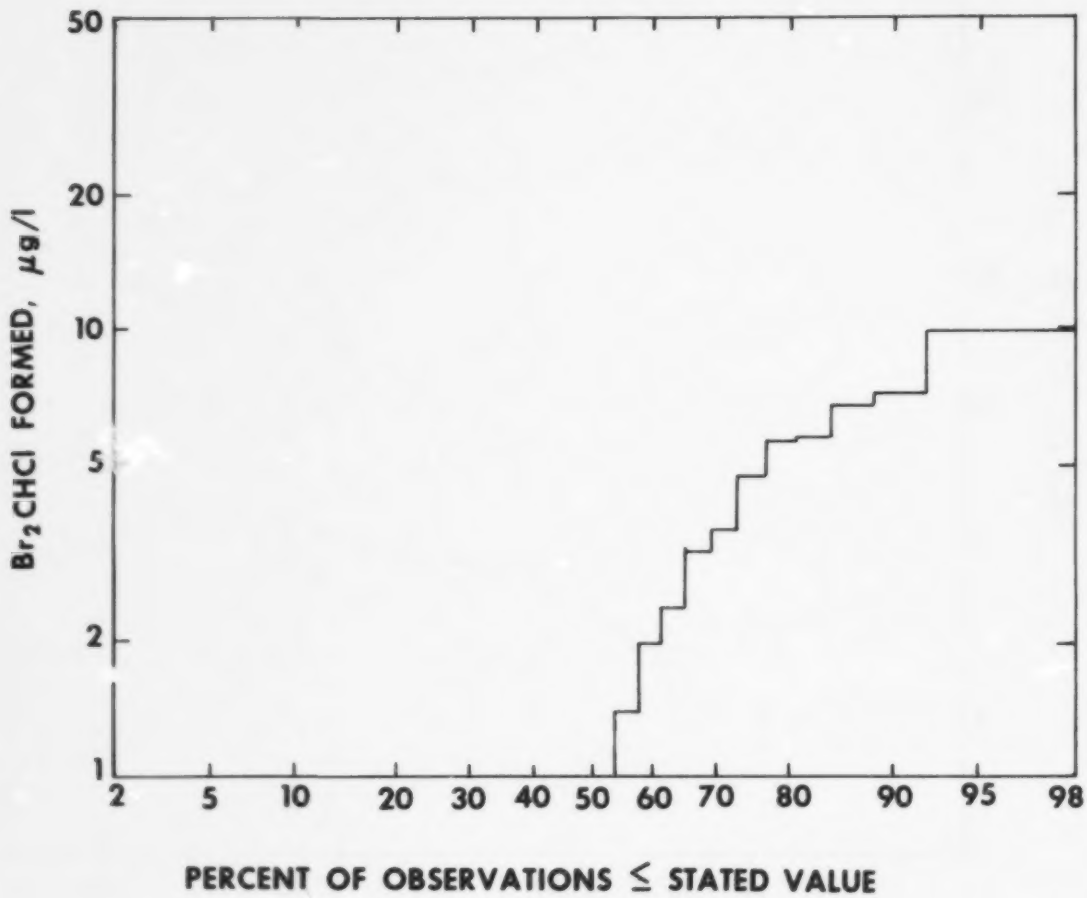

Figure A8. Br_2CHCl formed during chlorination of GMF effluent.

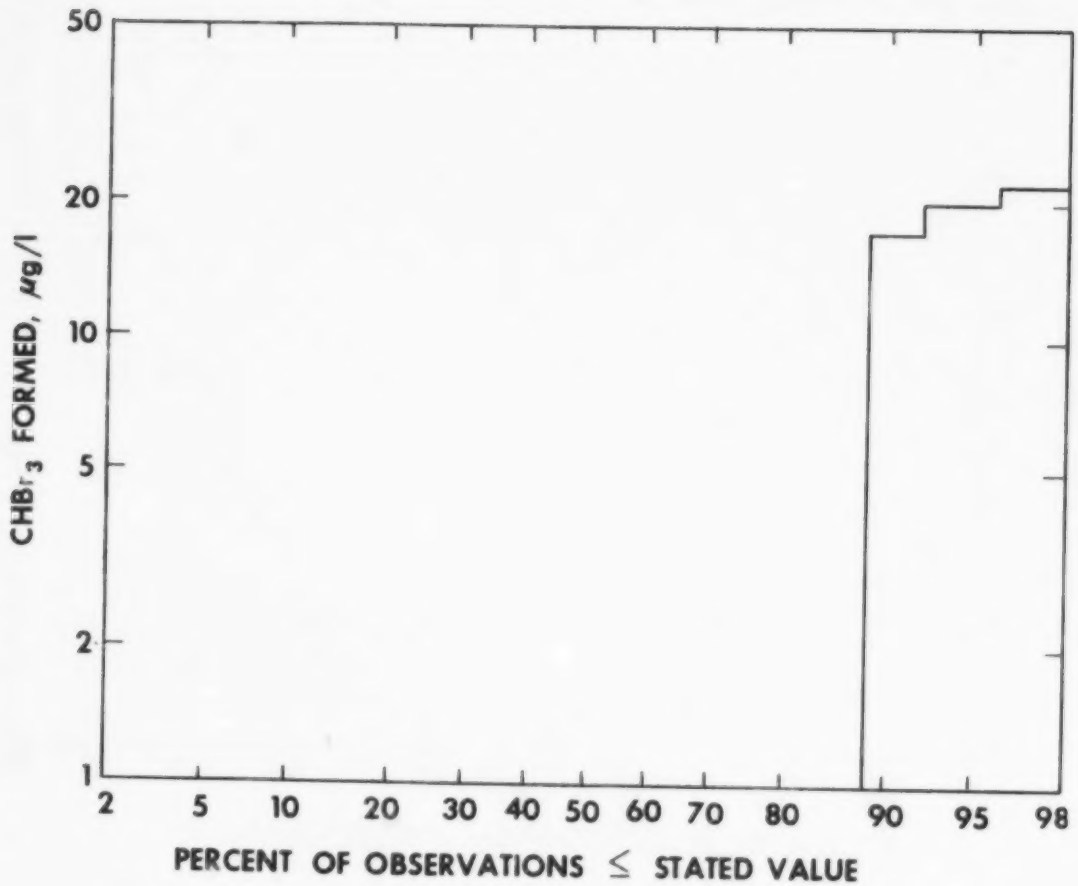

Figure A9. $CHBr_3$ formed during chlorination of GMF effluent.

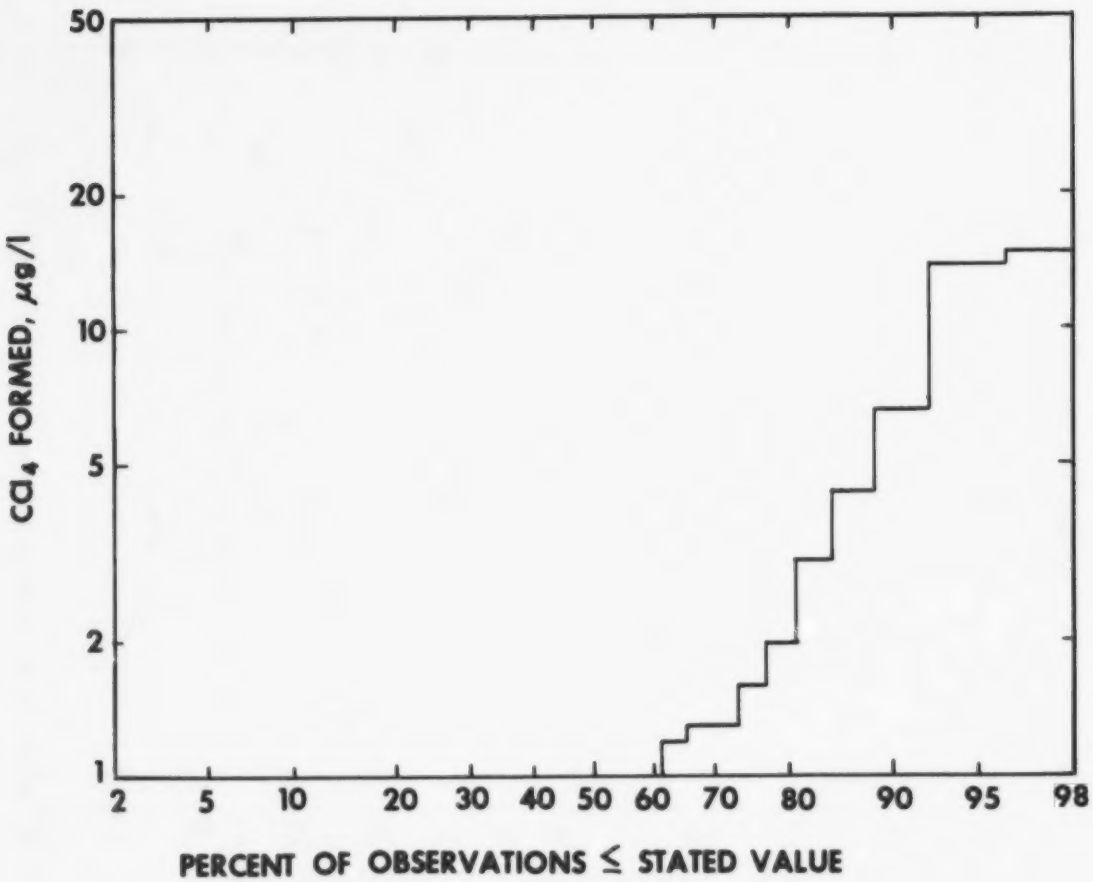

Figure A10. CCl_4 formed during chlorination of GMF effluent.

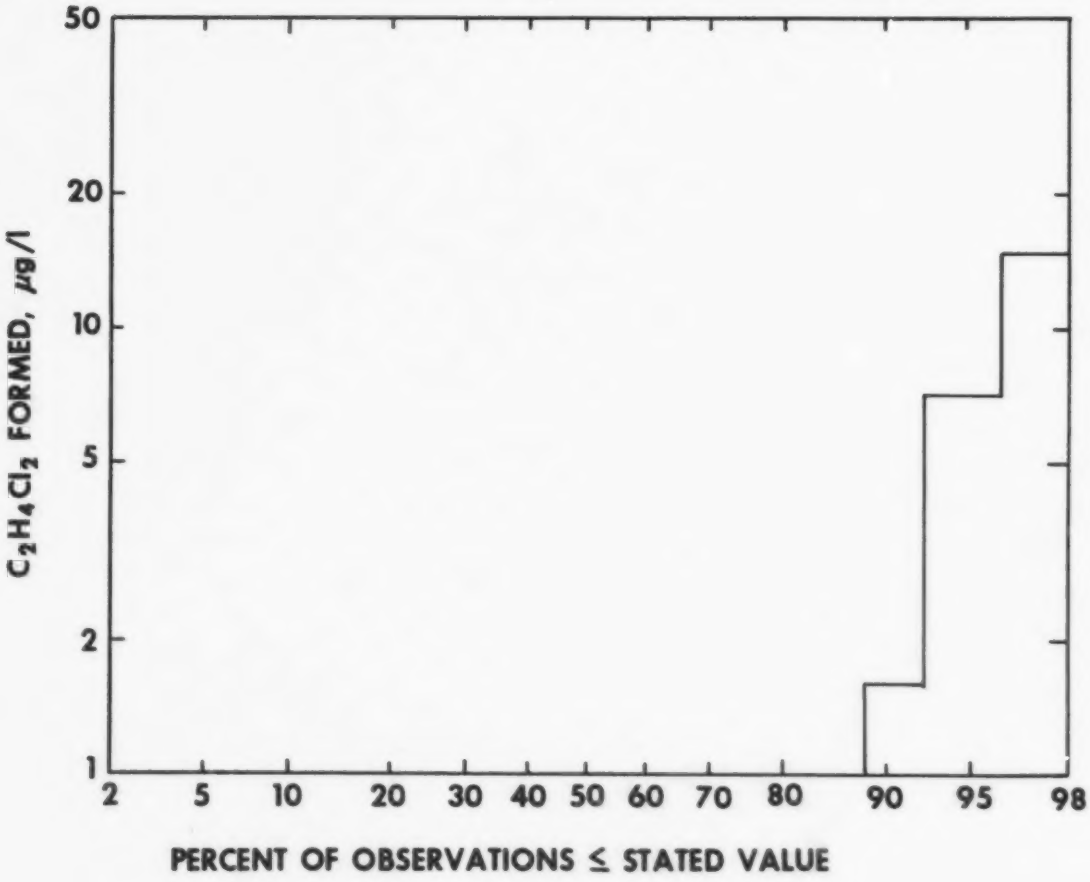

Figure A11. $C_2H_4Cl_2$ formed during chlorination of GMF effluent.